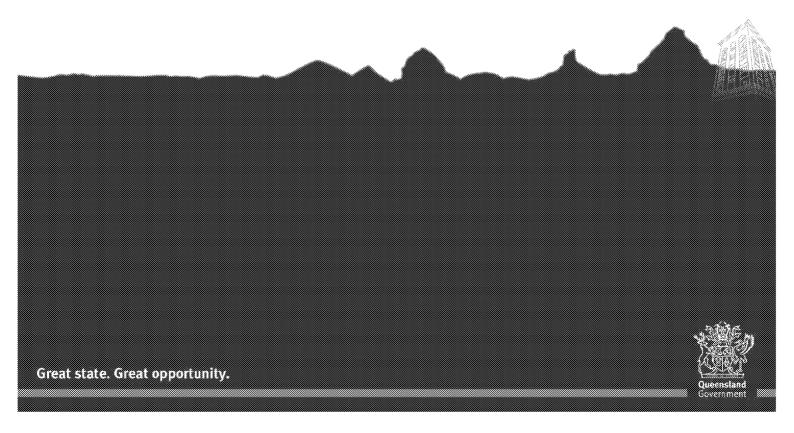
Managing Firefighting Foam Policy

Explanatory Notes



Prepared by: Incident Response Unit, Department of Environment and Heritage Protection

© State of Queensland, 2014.

The Queensland Government supports and encourages the dissemination and exchange of its information. The copyright in this publication is licensed under a Creative Commons Attribution 3.0 Australia (CC BY) licence.



Under this licence you are free, without having to seek our permission, to use this publication in accordance with the licence terms. You must keep intact the copyright notice and attribute the State of Queensland as the source of the publication.

For more information on this licence, visit http://creativecommons.org/licenses/by/3.0/au/deed.en

Disclaimer

This document has been prepared with all due diligence and care, based on the best available information at the time of publication. The department holds no responsibility for any errors or omissions within this document. Any decisions made by other parties based on this document are solely the responsibility of those parties. Information contained in this document is from a number of sources and, as such, does not necessarily represent government or departmental policy.

Version 1.3 – December 2014 www.EHP.qld.gov.au ABN 46 640 294 485

Contents

1	Introduction	1
	1.1 Background	1
	1.2 Firefighting foam	1
	1.3 Principles	2
2	Impacts of firefighting foams	3
	2.1 Composition of firefighting foams	3
	2.2 Biochemical oxygen demand (BOD)	7
	2.3 Biodegradability	8
	2.4 Acute (short-term) toxicity	9
	2.5 Persistence	9
	2.5.1 Persistence of fluorinated organic compounds	10
	2.5.2 Precursors and partial degradation of fluorinated organic compounds	11
	2.6 Bioaccumulation	12
	2.7 Chronic (long-term) toxicity	13
	2.8 PBT (Persistence-Bioaccumulation-Toxicity)	14
	2.9 Health, safety, amenity and economic considerations	15
	2.9.1 The costs of incidents involving firefighting foam	16
	2.9.2 Human health and safety implications	17
3	Treatment and disposal of wastes	18
	3.1 Firewater and wastewater treatment	
	3.2 Foam concentrate disposal	19
	3.3 Infrastructure contamination	20
4	Foam use issues	20
	4.1 Fire brigades	20
	4.2 Hydrocarbon refineries and large storage facilities	21
	4.3 Ports, shipping and offshore facilities	
	4.4 Mobile plant and hand-held extinguishers	23
5	Assessment standards and information	
	5.1 Safety Data Sheets (SDS/MSDS)	24
	5.1.1 SDS preparation	
	5.1.2 Ecological information (SDS Section 12)	
6	Balancing considerations	
	6.1 Large-scale release risks	
	6.2 Small-scale releases	27
	6.3 Considering the choices	
7	Use of persistent organic compounds	
	7.1 World-wide concerns	
	7.2 Ongoing use of fluorinated compounds	30
	7.3 U.S. EPA PFOA Stewardship Program relevance	31
	7.4 Long-chain fluorinated organic compounds	32
	7.5 Short-chain fluorinated organic compounds	33
	7.6 Alternatives to fluorinated compounds	35
	Use of non-persistent foams	
9	Policy implementation	37
	9.1 General compliance timelines	38
	9.2 Up to two years for large facilities to comply	38
D.	afarance	20

Managing Firefighting Foam Policy Explanatory Notes

1 Introduction

These Explanatory Notes provide background and clarification to the Management of Firefighting Foams Policy document and should be read in conjunction with that Policy.

There has been very significant evidence emerging in recent years regarding the potential for firefighting foams to have detrimental effects on environmental and other values during incident responses, training, maintenance activities and waste disposal when handled improperly and released to the environment via air, bodies of water, soils and groundwater.

Existing environmental legislation in Australia requires that any person, corporation or organisation carrying out an activity must take all reasonable and practicable measures to prevent or minimise the potential for environmental harm or pollution, having regard to the current state of technical knowledge for the operation or activity and other relevant matters.

The state-of-knowledge regarding the potential for firefighting foams to cause adverse effects on health and the environment has improved significantly in the last decade, as has the development of technologies and procedures to mitigate these effects. There now needs to be a consolidation of information and standards to guide users towards achieving best practice and ensuring that appropriate protective measures are taken and the liabilities for health, the environment and the user are properly assessed and managed.

1.1 Background

A significant review has been undertaken by the Queensland Department of Environment and Heritage Protection in conjunction with the Western Australian Department of Environmental Regulation into the potential impacts of the use of firefighting foams. This has included a very extensive literature review and consultation with regulators and experts in Australia and overseas.

The Foam Management Policy sets out foam management standards that must be met, the baseline information that must be provided and relevant test standards so that users, regulators and incident responders have a reasonable basis on which to make appropriate comparisons, decisions and choices when it comes to selecting a firefighting foam for any particular situation and to be able to plan for, and respond to incidents so that environmental and other values are least likely to be compromised.

While the review and the development of the Policy have primarily focussed on the potential for environmental harm or pollution to be caused, they also take into consideration human health impacts, workplace health and safety, firefighting performance, public amenity and economic issues.

Consultation with a range of stakeholders on the draft Policy raised a variety of general and specific issues, and additional information which has been considered in redrafting of the Policy and in the coverage and content of these Explanatory Notes.

1.2 Firefighting foam

Firefighting foam refers to concentrates and their aqueous solutions that are used in the production of streams or blankets of air/gas-filled bubbles to suppress flammable vapours,

increase water penetration, reduce static spark generation, control or extinguish fires, and prevent re-ignition by excluding air and cooling the fuel.

Firefighting foams may be used to prevent or extinguish fires involving:

- Class A fires in carbonaceous combustible materials, such as wood, paper, fabric, plastics and rubber, where the fire can be deep-seated in the burning material.
- Class B fires of flammable and combustible liquids or spills such as liquid hydrocarbon fuels and polar solvents where the fire and vapours are on the surface of the liquid.

Foam for these hazards and fires can be supplied by fixed piped systems or portable foamgenerating systems and be applied by methods such as portable hose streams using hand-held foam nozzles, large-capacity monitor nozzles or subsurface injection systems [1].

For the purposes of this review and the Policy the terms *Class A foam* and *Class B foam* are used to refer to the foams formulated for dealing with Class A and Class B fires respectively. Where the term *firefighting foam* is used it refers to both Class A and Class B foams unless specified.

1.3 Principles

The use of any firefighting foam has the potential to have a combination of environmental, health and economic impacts and it is ultimately the end-user that will bear the range of risks and liabilities associated with its albeit infrequent use.

When deciding on the most appropriate foam for a particular application, and whether or not current systems are adequate, the user needs to carefully consider the full range of short-term and long-term risks and factors that influence how they can achieve and demonstrate best practice [2] in the balance of the options for protection of *Life-Environment-Property*.

Firefighting systems need to be thought of in terms of not only their day-to-day utility and firefighting performance during incidents but also in terms of the entire lifecycle cost [3] including the potential downstream acute and chronic effects of releases on the environment, human health and amenities. It is acknowledged that every situation is different and to achieve the appropriate balance the user needs to take into consideration:

- Firefighting performance for the particular application.
- Adjacent environmental values (e.g. wetlands, bodies of water, soils, groundwater, etc.).
- Adjacent urban, amenity and economic values that could be impacted.
- Pathways for contaminants to affect adjacent values.
- The particular foam formulation (every foam is unique in its composition).
- Potential impacts of available firefighting system and foam options.
- Ability to capture, contain and treat wastes and firewater.
- Operational practicalities and compatibilities.
- Workplace health and safety (day-to-day and during incidents).
- Compliance with regulatory requirements and standards.
- · Potential costs for clean-up and harm or pollution caused on and off site.
- Costs and practicalities of waste treatment and disposal.
- Corporate reputation and liability.
- Value for money through a cost-benefit analysis.

There will never be a "one-size-fits-all" firefighting foam system that achieves all-round best-practice protection for all circumstances and considerations. In attempting to properly assess the risks inherent in their situation and to make a confident and informed choice when selecting an appropriate system and foam, users are often significantly hampered by a lack of information, incomplete knowledge and inadequate and/or inaccurate advice in one or more relevant areas.

The benchmark for overall best-practice in firefighting foam formulations and their use has changed progressively in recent years. Increasing awareness of the adverse health and environmental effects associated with some compounds in formulations, which were previously

regarded as acceptable or were the only available effective solution at the time, has in particular driven the need for continuous improvement and development of better practices and formulations with more acceptable health and environmental outcomes.

This now means that many users need to reassess their risks and liabilities and, where necessary, improve their performance against current and emerging best practice. In some cases this can be easily achieved but for some foam users this represents a significant operational and cultural challenge.

In addition to the increased knowledge about the behaviour and effects of pollutants generally there is now also a greater expectation by the community that health, amenity and environmental values will be properly considered and protected with decisions based on comprehensive and balanced risk assessments that take all relevant factors into account.

2 Impacts of firefighting foams

All firefighting foams are of concern if they are released to the environment; there is no such thing as a completely "environmentally friendly" foam as espoused in some marketing brochures. Firefighting foams depend on a variety of compounds and formulations for their effectiveness. Some of the compounds and formulations can have adverse short and long-term impacts on the environment, human health and other values if released. The primary areas of concern are:

- Biochemical oxygen demand The majority of foams have high BOD potential. Dissolved oxygen levels in water can be quickly and severely depleted when the organic components of released foam are degraded by the action of naturally occurring aerobic micro-organisms.
- Acute (short-term) toxicity Toxicity from detergents, solvents and other components in foams can result in immediate adverse effects on organisms in the area of the release.
- Persistence Foams may contain compounds of known, suspected and currently unknown toxicity that do not degrade in the environment and/or are not readily metabolised in biota and can therefore exert potential toxic effects over a long period of time. Persistence also means that there is an increased risk of long-term exposure, bioaccumulation of toxic compounds and dispersal with impact on areas, some at great distances from the source of the discharge.
- Bioaccumulation The uptake of toxic compounds by organisms and the accumulation of them at higher concentrations than in the environment and the potential for the compounds to be passed up, and further bioconcentrated up the food chain (trophic magnification).
- Chronic (long-term) toxicity The often overlooked potential for compounds to cause long-term impacts on humans and organisms, especially if they are persistent and/or bio-accumulative, even though their short-term toxicity may be relatively low.

2.1 Composition of firefighting foams

While the composition of firefighting foams includes general classes of compounds, such as surfactants, solvent, stabilisers and thickeners, each foam formulation is unique and differs in the combination of specific ingredients. The potential for adverse health and environmental effects depends on the physical and toxic effects of particular ingredients as well as the synergistic effects of them in combination in the formulation.

For example, a biocide or preservative that is not critical to firefighting performance may have particular toxic effects in the environment that may be enhanced or suppressed when in combination with other unrelated compounds.

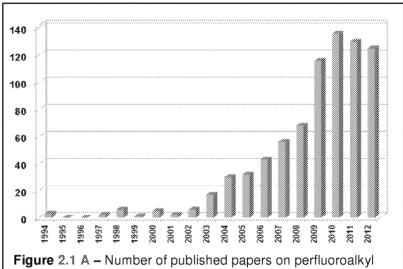
Fluorinated organic compounds have been a common ingredient in firefighting foams for many decades, being the key to the properties and effectiveness of many foams. There has been a growing awareness in recent times of the potential for very significant, long-term and widespread adverse human health and environmental effects of these compounds, with the result that this

has brought them under particular scrutiny and has driven a reassessment of their use, fate and effects.

The growth in knowledge about the behaviour and effects of fluorinated organic compounds is illustrated by the number of papers published from 1994 to 2012 on environmental aspects of these compounds (Figure 2.1 A) [4].

This shows the recent rapid increase in interest and information about fluorinated organic compounds over the last decade but also illustrates the almost complete lack of knowledge in the public domain about the environmental (and probably health) effects between the time of their first use in the 1960s to the early 2000s.

PFOS and PFOA are the most often mentioned fluorinated organic compounds and are well recognised as being of serious concern for human health and the environment [5.6,7,8] (Policy Section 3.1.2).



substances 1994 to 2012 (Redrawn from Trojanowicz & Koc [4])

The casual reader could be forgiven for thinking that PFOS and PFOA are the only two compounds of concern [9,10]. It is very important, however, to realise that there are thousands of possible fluorinated organic compounds [11,4], and of those in use in some firefighting foams only about 50 have been publicly identified so far [12,13,14] with a similar or greater number of others currently remaining unidentified [15.16].

In a 2013 study of 12 samples of foam used in Canada [17,15] (and elsewhere) comparison of the concentrations of known fluorosurfactants with the total organofluorine content found less than 10% of the fluorosurfactants were identified in half of the samples and generally less than 50% of fluorinated organic compounds were identifiable overall (in some samples 0% were identified). PFOS was also a significant component in 6 of the 12 samples.

This has very significant implications for risk assessment of the possible environmental effects of these as well as other fluorinated foams if these results are typical as a very significant proportion of the fluorinated organic compounds used are largely unknown and undeclared in Safety Data Sheets (SDS) or elsewhere. Consequently the behaviour, impact and fate of those fluorinated compounds in the environment are largely unable to be assessed.

There are two main groups of fluorinated organic compounds. These materials are commonly termed per-fluoroalkyl and poly-fluoroalkyl substances (collectively the PFASs) [9] and it is important to appreciate the difference between poly-fluorinated and per-fluorinated compounds (Figure 2.1 B), their occurrence in foams and how they subsequently behave in the environment:

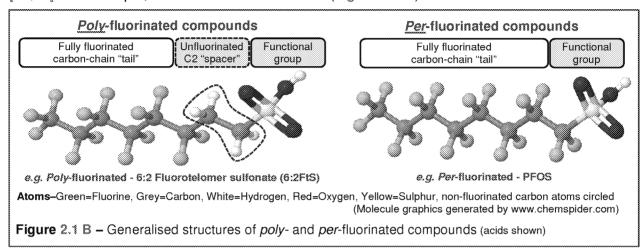
- Per-fluorinated compounds such as PFOS and PFOA, where all the atoms in the main carbon chain are fluorinated and do not hydrolyse, photolyse, or biodegrade under environmental conditions.
- Poly-fluorinated compounds such as 8:2 fluorotelomers that have carbon atoms in the chain that are not fully fluorinated but on release to the environment will partially degrade resulting in a per-fluorinated end-point compound.

Where the compound is described as an X:Y fluorotelomer the "X" denotes the number of fully or per-fluorinated carbon atoms and the "Y" denotes the number of non-fluorinated carbon atoms [9,18]. The general structure of poly-fluorinated compounds consists of three groups [19]:

- an oleophobic/hydrophobic fully-fluorinated carbon-chain tail, (CF₃-CF₂-CF₂-...)
- a non-fluorinated organic "spacer" (dimethylene group, -CH₂-CH₂-)
- a hydrophilic functional group (sulfonate, betaine, carboxylate, etc.).

Per-fluorinated compounds do not have the middle, unfluorinated spacer group.

Fluorotelomers compounds are commonly composed of a straight-chain with an even number of fluorinated carbons (C6, C8, C10, etc.) with the unfluorinated C2 dimethylene group (-CH₂-CH₂-) between the fluoralkyl chain and the end group that determines the compound's functionality [18,20]. For example, 6:2 fluorotelomer sulfonate (Figure 2.1 B) or 8:2 fluorotelomer betaine.



Tables 2.1 A & 2.1 B illustrate the diversity and complexity of some of the fluorinated organic compounds thus far identified as occurring in fluorinated foams or resulting from partial degradation. This is further complicated by some compounds also being able to exist as different structural arrangements of branched and unbranched isomers. PFOA (C₈HF₁₅O₂), for example, has 39 possible structural isomers, that is, 39 different arrangements of the chain lengths and branches for the same molecular composition [21].

Additionally, those fluorotelomers with eight carbons in the perfluorinated chain (e.g. 8:2FtS), including some found in foams advertised to be "PFOS and PFOA free", will partially degrade in the environment relatively quickly producing PFOA as the major end-point perfluorinated degradation product [22,23,24]. A similar process occurs for the larger, more toxic higher homologue compounds such as 10:2FtS which degrades to perfluoro decanoic acid (PFDA) (Figure 2.5.1 A). Such compounds that degrade to a perfluorinated compound are termed precursor compounds e.g. PFOA precursors or PFOS precursors.

Place & Field (2012)-FOCs in MilSpec AFFF [12]			
Perfluorobutane sulfonamide amine (C4)	4:2 fluorotelomer sulfonamide betaine		
Perfluoropentane sulfonamide amine (C5)	5:1:2 fluorotelomer betaine		
Perfluorohexane sulfonamide amine (C6)	5:3 fluorotelomer betaine		
Perfluorobutane sulfonamide amino carboxylic acid (C4)	7:1:2 fluorotelomer betaine		
Perfluoropentane sulfonamide amino carboxylic acid (C5)	7:3 fluorotelomer betaine		
Perfluorohexane sulfonamide amino carboxylic acid (C6)	8:2 fluorotelomer sulfonamide amine		
Perfluorohexane sulfonamide ammonio dicarboxylic acid	8:2 fluorotelomer sulfonamide betaine		
Perfluoropentane sulfonamide ammonio dicarboxylic acid	8:2 fluorotelomer thio hydroxy ammonium		
Perfluorohexane sulfonic acid (PFHxS)	8:2 fluorotelomer thioether amido sulfonic acid		
Perfluoroheptane sulfonic acid (C7 PFHpS)	8:2 fluorotelomer thioether amino carboxylic acid		
Perfluorooctane sulfonic acid (C8 PFOS)	9:1:2 fluorotelomer betaine		
6:2 fluorotelomer sulfonamide amine	9:3 fluorotelomer betaine		
6:2 fluorotelomer sulfonamide betaine	10:2 fluorotelomer sulfonamide betaine		
6:2 fluorotelomer thio hydroxy ammonium	10:2 fluorotelomer thioether amino carboxylic acid		
6:2 fluorotelomer thioether amido amino carboxylic acid			
6:2 fluorotelomer thioether amido sulfonic acid			

Table 2.1 B - Fluorinated organic compounds (FOCs) in samples of firefighting foams and groundwater				
Backe, Day & Field (2013)–FOCs in AFFF and groundwater [13]				
4:2 fluorotelomer thioamido sulfonate	Perfluoroheptyl carboxylate (C7)			
6:2 fluorotelomer thioamido sulfonate	Perfluorooctyl carboxylate (C8 PFOA)			
8:2 fluorotelomer thioamido sulfonate	Perfluorononyl carboxylate (C9)			
4:2 fluorotelomer sulfonate (4:2FtS)	Perfluorodecyl carboxylate (C10)			
6:2 fluorotelomer sulfonate (6:2FtS)	Perfluoroundecyl carboxylate (C11)			
8:2 fluorotelomer sulfonate (8:2FtS)	Perfluorododecyl carboxylate (C12)			
Perfluoroheptly sulfonamido amine (C7)	Perfluorotridecyl carboxylate (C13)			
Perfluorooctyl sulfonamido amine (PFOS precursor [25])	Perfluorotetradecyl carboxylate (C14)			
Perfluorheptyl sulfonamide amino carboxylate (C7)	(Fluorinated organic compounds common to both studies)			
Perfluoroctyl sulfonamide amino carboxylate (C8)	(6:2 fluorotelomer thio hydroxy ammonium)			
Perfluorobutyl sulfonamido amine (C4)	(6:2 fluorotelomer sulfonamido betaine)			
Perfluoropentyl sulfonamido amine (C5)	(8:2 fluorotelomer sulfonamido betaine)			
Perfluorohexyl sulfonamido amine (C6)	(10:2 fluorotelomer sulfonamido betaine)			
Perfluorbutyl sulfonamide amino carboxylate (C4)	(12:2 fluorotelomer sulfonamido betaine)			
Perfluorpentyl sulfonamide amino carboxylate (C5)	(5:1:2 fluorotelomer betaine)			
Perfluorohexyl sulfonamide amino carboxylate (C6)	(7:1:2 fluorotelomer betaine)			
Perfluorobutyl sulfonate (C4 PFBS)	(9:1:2 fluorotelomer betaine)			
Perfluoropentyl sulfonate (C5 PFPeS)	(5:3 fluorotelomer betaine)			
Perfluorononyl sulfonate (C9 PFNS)	(7:3 fluorotelomer betaine)			
Perfluorodecyl sulfonate (C10 PFDS)	(9:3 fluorotelomer betaine)			
Perfluorobutyl carboxylate (C4)	(Perfluorohexyl sulfonate (C6))			
Perfluoropentyl carboxylate (C5)	(Perfluoroheptyl sulfonate (C7))			
Perfluorohexyl carboxylate (C6)	(Perfluorooctyl sulfonate (C8 PFOS))			

In general the focus of concerns for fluorinated organic compounds used in firefighting foams has been on perfluorinated compounds such as PFOS and PFOA, plus a range of X:Y fluorotelomers which each have various different effects in their own right, as well as being precursors for a number of other compounds due to partial degradation.

In addition to these commonly discussed compounds other variants of fluorinated organic compounds are of similar concern, regarded as having the same potential effects and producing similar breakdown and transformation products as the fluorotelomers and perfluorinated compounds [13,12,26,9,27] including:

- X:Y:Z fluorotelomers indicating \underline{X} fully-fluorinated, \underline{Y} singly-fluorinated carbons, and \underline{Z} non-fluorinated carbon atoms prior to the first functional group (e.g. 9:1:2 fluorotelomer betaine).
- Fluoro-polymers e.g. substituted in foam for fluorotelomers and perfluorinated compounds.
- Substituted halogenated polyfluorocarbons and perfluoropolyethers [28,29] (e.g. chlorinated polyfluorinated ether sulfonate, C₈CIF₁₆O₄S⁻, which has similar characteristics, toxicity and behaviour to PFOS).

In regards to the use of fluoropolymers and their being considered in the same way as perfluorinated compounds and *X:Y* fluorotelomers, this is in line with the removal of the fluoropolymer exemption to the *Polymer Exemption Rule to Exclude Certain Perfluorinated Polymers* by U.S. EPA 2010 [30].

This exclusion refers to fluoropolymers containing, as an integral part of their composition, perfluoroalkyl moieties consisting of a CF_{3} - or longer chain length including perfluoroalkyl sulfonates (PFAS), perfluoroalkyl carboxylates (PFAC), fluorotelomers, or perfluoroalkyl moieties that are covalently bound to either a carbon or sulfur atom where the carbon or sulfur atom is an integral part of the polymer molecule. These fluoropolymers are now regarded as posing an unreasonable risk to human health or the environment.

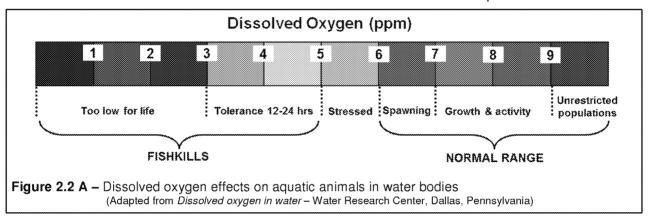
While the simple fluorinated homopolymers such as PTFE (Teflon®) are not of concern, the more complex branched copolymers have the potential to have similar effects to *poly*-fluoroalkyl and *per*-fluoroalkyl compounds or partially degrade to compounds of concern.

2.2 Biochemical oxygen demand (BOD)

Biochemical oxygen demand is a measure of the amount of oxygen consumed, primarily by aerobic bacteria, in breaking down organic matter in a water body (with some contribution from algal respiration, sediment and chemical uptake). The terms *biochemical* oxygen demand and *biological* oxygen demand are interchangeable for the purposes of the Policy.

Notwithstanding that compounds used in the formulation of firefighting foams may have separate acute and chronic toxic effects, the primary concern regarding the BOD potential of firefighting foam is that elevated BOD associated with degradation of organic components, such as glycols or glycol ethers, will result in rapid depletion of dissolved oxygen in a water body causing harm to aquatic life, mainly through asphyxiation.

The majority of foams have high potential BOD values (expressed as BOD for the concentrate) generally in the higher range between 1,500 mg/L to 450,000 mg/L. Given that the natural dissolved oxygen concentrations in bodies of water are relatively low, in the range of 6 mg/L to 9 mg/L (Figure 2.2 A), this means that there is significant potential for environmental harm even from the release of firewater derived from finished foam at 1% to 6% dilutions, particularly in confined bodies of water with limited volume and turnover to dilute and disperse contaminants.



From the foam user's perspective, as well as for the incident responder, when planning for responses it is highly desirable to put in place procedures and measures to contain and prevent or minimise the release of firewater (e.g. by containment in ponds, bunds or drains) for a sufficient period to allow degradation to occur before release such that the elevated BOD potential does not have any significant impacts on the adjacent bodies of water.

Usually the decomposition of the degradable organics introduced to a body of water can in many (but not all) cases be assumed to have proceeded to about 70% of the final value after 5 days (the BOD_5 value) [31] and is effectively complete after 20 to 28 days with no further significant BOD impacts likely [32,26].

While the BOD process in a body of water may be complete by about 28 days after the release, there may be a further lag while dissolved oxygen levels in the water return to normal, e.g. from additional BOD associated with dead vegetation present and/or a delay in return to a normal equilibrium for the biota in the waterway. Measurements of the recovery of dissolved oxygen levels back to normal concentrations in the water should be used to monitor progress.

When assessing the potential for BOD to affect dissolved oxygen levels in a body of water, say from SDS information, note that the standard BOD test is carried out at 20°C, therefore biodegradation can be expected to proceed more rapidly at higher water temperatures and will be slower at temperatures below 20°C.

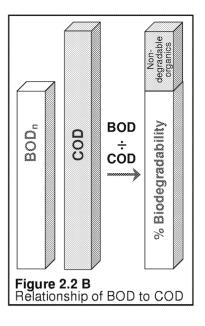
Chemical oxygen demand (COD) is not the same as BOD, BOD is a subset of COD (Figure 2.2 B). Both COD and BOD values must be cited for foam concentrate. COD is a measure of the theoretical maximum amount of oxygen required to oxidise all of the oxidisable organics in a sample (clearly excluding persistent organic compounds not oxidisable by the method or oxidisable in the environment), the COD test is carried out under relatively strong oxidising

conditions using acid dichromate. COD does not represent the degree of oxidation that will occur in the natural environment.

The ratio of BOD to COD represents the proportion of the organic components in a material that are readily biodegradable in the environment. At a minimum the values for COD, BOD₅ and BOD₂₈ should be cited in the SDS for foam concentrate to provide an indication of:

- immediate effects (≈BOD₅), i.e., acute oxygen stress
- overall oxygen demand (≈BOD₂₈ or BOD_n), i.e., a measure of the degradation burden
- overall biodegradability (BOD as a proportion of COD).

If the progressive natural degradation of the foam product is unusual then the SDS should cite a range of BOD values (e.g. 5, 10, 15, 20, 28 day) or the degradation BOD characteristics can be represented by a graph of BOD against a relevant time period of 28 days or more [32].



2.3 Biodegradability

In terms of the potential effects on the environment of a release of firefighting foam there needs to be consideration of the duration and severity of the effects of toxic compounds as well as the oxygen depleting BOD effects, which may be related to relatively non-toxic compounds.

Biodegradability is closely tied to BOD processes and describes the extent to which the organic components in a product will break down through natural processes in the environment and therefore the extent and duration of potential impacts of those compounds until they degrade.

The focus of biodegradability is mostly on the breakdown of the toxic components to non-toxic end-products such as salts, water and carbon dioxide, a process known as mineralisation. A large proportion of the compounds in firefighting foam are degradable organics such as glycol ether solvents and hydrocarbon surfactants which result in high overall biodegradability as judged from the ratio of BOD to COD (Figure 2.2 B). In many cases there is reliance on natural breakdown processes to break down toxic compounds and to remediate soils and water bodies over time.

The degradability of a product or waste under environmental or biological treatment conditions is generally determined as the ratio of the 28 day biochemical oxygen demand (BOD₂₈) to the total chemical oxygen demand (COD) of oxidisable organics, expressed as a percentage (BOD₂₈/COD x 100). However, this assumes that all the organic components are able to be oxidised in the standard COD method. In the case of fluorinated foams this does not take into account the non-degradable fluorinated organic compounds that cannot be readily oxidised as they are chemically extremely stable and resistant to oxidation by acid dichromate [26].

For the purposes of classifying and stating the biodegradability of a firefighting foam all the organic compounds in its composition must degrade under normal environmental conditions within 28 days from the time of its release to water by:

- >95% to be classed as readily biodegradable
- >99% to be classed as fully biodegradable.

Where some organic components eventually degrade, but are not readily or fully degradable within 28 days under environmental conditions, the period over which the organics degrade needs to be stated (e.g. "95% biodegradable over 45 days").

Where the foam contains persistent toxic organic compounds it cannot be described or implied as being readily or fully biodegradable even when the overall persistent organic compounds are <5% w/v in the concentrate or <1% w/w of the total organic components respectively.

Rapid and complete biodegradability is desirable for pollutants released to the environment even if the BOD is high and their acute toxicity is higher than less acutely-toxic but persistent alternatives.

2.4 Acute (short-term) toxicity

Acute toxicity refers to the immediate or short-term effects of contaminants; usually the effects occur within hours or days of exposure. Acute toxicity testing observes the effects of a contaminant over a short period, e.g. over 24 hours, relative to a single exposure at the beginning of the test procedure or the effects of exposure to particular concentrations [33].

Concerns regarding acute toxicity of foam releases focus on the potential to cause harm to aquatic organisms in bodies of water. Tests for acute toxicity usually involve aquatic test species such as crustaceans, algae and fish relevant to the location or at least tests that use standardised test species across the relevant groups.

The foam management Policy stipulates the standard test methodologies and information that must be made available so that users, regulators and incident responders have a basis for assessing the acute toxicity risks they face and make appropriate comparisons, decisions and choices. The Policy includes guidance on relevant test species and best-practice test methods. It should be noted that sensitivity to toxins is variable across species and assumptions cannot be made even within related groups such as fish and crustaceans [34.35].

Significant problems have arisen for foam users, environmental regulators and incident responders in that acute ecological toxicity test data and information reported in foam product information and safety data sheets are rarely adequate, or are even completely absent, making it difficult or impossible for the user to make an informed judgement or decision in regard to a balanced environmental risk assessment for response planning or incident management.

Quite often acute ecological toxicity information cited in the SDS and product information only relates to selected components of the foam and is not for the final product formulation. It is well recognised that the overall toxicity of mixtures may be very different from its separate ingredients [36,37] through largely unpredictable synergistic effects between components. For acute toxicity test results to be relevant the tests must be done for the final product formulation and at the usage concentration, it is not sufficient, and is very often misleading, only to report on selected components in isolation.

Manufacturers/suppliers may choose to provide additional information in SDS and product technical information beyond that required by the Policy. Equally, users may need to seek further information relevant to particular or unusual circumstances that they face or for the environment in which the foam will be used (such as the near-shore marine environment) before deciding how best to address their needs and obligations.

2.5 Persistence

The presence of any persistent toxic compounds in releases to the environment is of concern. Toxicity effects on health and the environment can be exerted over a long period with the added possibility that bioaccumulation and long-range dispersal may occur [38,39,40,41,8]. The term *persistence* in the Policy is used to mean environmental persistence; it should not be confused with bio-persistence (see Section 2.8).

Firefighting foams are often used in situations where containment may be difficult, so it is likely that there will be releases to the environment and dispersal under a variety of circumstances. This could occur on a large or small scale during incidents and normal operational activities. Where persistent toxic compounds are present, care must be taken to ensure that the likely environmental risks and impacts are *fully understood* and such products are only used with appropriate containment and controls in place.

Many pollutants released to the environment can be expected to naturally degrade over time or to become immobilised, (e.g. by adsorption to sediments, microbial degradation, oxidation,

reduction, hydrolysis, UV photo-degradation, hydroxyl attack in the atmosphere, etc.). However, fluorinated organic compounds do not naturally diminish in this way as might normally be expected due to their extreme persistence, solubility, high mobility, high acid strength (low pKa) and dispersibility of volatile precursors or breakdown products in air (such as FTOHs or short-chain perfluoroalkyl derivatives from landfill or WWTP emissions), in water and in soil [42,43,9,44,45,14].

Extreme persistence in itself is not a primary problematic characteristic but when the compounds or their degradation products are also toxic, highly dispersible, and may be biopersistent and bioaccumulative, even compounds that have short-term low to moderate toxicity require very close scrutiny for the potential for adverse health and environmental effects to occur over the longer term and make a conservative approach to management necessary, i.e. the application of the precautionary principle [26,3]. Environmental persistence increases the risks of toxicity, biopersistence, bioaccumulation, bioconcentration and biomagnification occurring.

An organic compound is considered environmentally *persistent* (*P*) or *very persistent* (*vP*) under *Annex XIII of REACH* (*EC 2011*) when its half-life, including that of its degradation products with similar characteristics or effects, is greater than those shown in Table 2.5 A for each environmental compartment.

Table 2.5 A – Criteria for identifying Persistent (P) and Very Persistent (vP) substances [46]					
Persistent (P) degradation half-life		Very Persistent (vP) degradation half-life			
Marine water	>60 days	Marine water	>60 days		
Fresh or estuarine water	>40 days	Fresh, or estuarine water	>60 days		
Marine sediment	>180 days	Marine sediment	>180 days		
Fresh or estuarine sediment	>120 days	Fresh, or estuarine sediment	>180 days		
Soil	>120 days	Soil	>180 days.		

2.5.1 Persistence of fluorinated organic compounds

Many firefighting foams are heavily reliant on longer-chain (>C6) fluorinated organic compounds for their firefighting performance and these foams have been extremely effective in a range of firefighting applications with few alternatives available until recently.

Since about 2000 there has been growing and significant evidence of the adverse health and environmental effects of poly- and per-fluorinated organic compounds released from various sources including fabric protectants and manufacturing processes as well as firefighting foams. Perfluorinated organic compounds are well known to be extremely persistent in the environment, with no known natural processes whereby they will degrade [22,11,6,42,47,8].

The extreme persistence of perfluorinated organic compounds can be described as "geological" to the extent that rock strata in the distant future, formed from current contaminated sediments, are likely to contain un-degraded perfluorinated organic compounds from releases in the last few decades as complete mineralization is not expected to occur under natural conditions [48,49]. In addition, fluorinated organic compounds are also likely to be still circulating in the environment after similar very long periods of time. For example, the simplest perfluoroalkyl compound, fluoro-methane (CF₄), has an estimated half-life in the upper atmosphere of >50,000 years [50].

The carbon-fluorine bond in fluorinated organic compounds is extremely strong and stable, it is the strongest bond in organic chemistry [7,9,51,52], enhanced by overlapping electron shells and a short C-F bond length [45]. This gives extreme durability to perfluorinated organic compounds under all but exceptional chemical and physical conditions. It is not surprising that perfluorinated organic compounds do not undergo biotic or abiotic degradation under environmental conditions given that even thermal degradation only occurs at temperatures of about 1,100°C with at least 2 seconds residence time at that temperature [53,24,54,55].

Normally persistence or degradation in the environment is described in terms of a compound's *half-life*, being the time it takes for 50% of the original amount or concentration of the compound to degrade. The environmental half-life of PFOA has been described as "*challenging or even*"

impossible to measure" with an estimate of PFOA's half-life under artificial hydrolysis conditions in the laboratory of about 92 years [22]. Even under these artificial conditions the expected degradation of PFOA to a residual amount below 1% of the original concentration would be seven half-lives or about 644 years.

Another estimate puts the half-life of PFOA under hydrolysis at about 235 years [41] giving an expected time to degradation below 1% of about 1,645 years. These estimates are purely notional as PFOA persistence, and that of all similar perfluorinated organic compounds, is expected to be effectively indefinite under environmental conditions.

2.5.2 Precursors and partial degradation of fluorinated organic compounds

While *per*fluorinated compounds will not degrade under environmental conditions, fluorotelomers such as 8:2 FtS have part of the carbon chain (the dimethylene group) that is not fully fluorinated and on release to the environment will *partially degrade*, however their end-point degradation products are still highly persistent perfluorinated compounds related to the fully fluorinated part of the carbon chain (Figure 2.5.1 A) [21,25], for example:

- In the case of a variety of 8:2 fluorotelomers the end point is the carboxylic acid PFOA, after the non-fluorinated -CH₂-CH₂- dimethylene group is lost.
- For higher homologue 10:2 fluorotelomers the end point is perfluorodecanoic acid (PFDA).
- For compounds such as perflourooctyl sulfonamides the partial degradation end-point is likely to be PFOS.

From an environmental standpoint it is highly misleading to describe fluorinated organic compounds as "degradable" which implies in general parlance to the non-specialist end-user that the product fully degrades and therefore it might be assumed that there are no residual persistent end-compounds of concern. This is not the case.

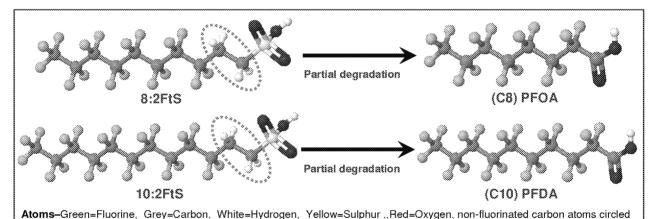


Figure 2.5.1 A – Degradation of 8:2 and 10:2 fluorotelomer compounds to PFOA and PFDA (The sulfonic acid –HSO₃ functional group shown in the example *X:Y* compounds is notional. A range of other functional groups can occur instead such as betaine, sulfonamide amine, etc. with the same degradation end-points of PFOA and PFDA). (Molecule graphics generated by www.chemspider.com).

The "degradation" of fluorinated organic compounds under environmental conditions only refers to the partial degradation or loss of the non-fluorinated carbons (usually a C2 dimethylene group) from some compounds and also, under specific conditions, limited partial de-fluorination adjacent to non-fluorinated carbon atoms, ultimately (and possibly through intermediate steps) leaving behind a persistent per-fluorinated compound. This process may also involve a transformation where the functional group changes, e.g. a sulfonamide is replaced by a sulfonate.

The eventual end-point compound left behind by partial degradation is a highly persistent perfluorinated compound which does not degrade under environmental conditions [56,47,45]. The partial degradation/transformation steps and their intermediate compounds (and their half-lives) that lead to the eventual end-point compound, and the environmental behaviour of each of these compounds, are also not well understood. This applies to both long-chain and short chain compounds [15,27,47].

Foams containing significant concentrations of PFOA precursor compounds such as 8:2 fluorotelomers effectively leave the user unwittingly exposed to the liability of having released foam that relatively quickly generates PFOA with a very significant potential to cause health and environmental impacts.

Similarly, those foams with significant concentrations of longer-chain fluorotelomers, such as 10:2FtS and 12:2FtS or equivalents ([13,25] and Tables 2.1 A & B), will partially degrade to C10 perfluorodecanoate (PFDA) and C12 perfluorododecanoate respectively. These are higher homologues of PFOA which are orders of magnitude more toxic and more bioaccumulative [40].

Given the relatively rapid degradation of 8:2 fluoroteleomers to PFOA in the environment the release of foam that contains these PFOA precursor compounds is effectively regarded as a release of PFOA to the environment as the PFOA precursor compounds can have relatively short half-lives (e.g. as short as 10.3 days for 8:2 fluorotelomer stearate monoester [57]). Similarly perfluorooctyl sulfonamido amine in a foam is likely to degrade to PFOS amongst at least 96 other PFOS precursor substances [45].

Effectively some foams advertised as "PFOA and PFOS free" may not remain PFOS or PFOA-free for very long once put into use and partial degradation occurs.

Under the Policy foams containing PFOA and/or its precursors and their higher homologues are required to be withdrawn from service as soon as it is practicable and disposed of properly. It is recognised that a significant number of firefighting foams in service are currently dependent upon PFOA precursor fluorinated organic compounds (as well as very significant levels of the more toxic longer-chain C10 and C12 compounds [13,16]) and that a reasonable time to transition to alternative foams will be required; this will vary according to the complexity of the particular circumstances.

Firefighting foams that contain significant levels of PFOS (>10 mg/kg), its higher homologues and their precursors are of *very significant concern* for human health and the environment and as such the Policy requires that they are not to be used and must be withdrawn from service *immediately*, secured and arrangements made for proper disposal [\$3,58]. The potential for adverse health and environmental effects by PFOS has been well understood for some considerable time.

2.6 Bioaccumulation

Bioaccumulation is the general and continued uptake of substances from the environment through contact, with nutrient uptake and through diet resulting in an increasing concentration within the organism which increases the potential for health and environmental harm to occur substantially, especially in the case of toxic, highly persistent compounds that are not metabolised or are slow to be eliminated from animals.

In a general sense the term bioaccumulation also encompasses the related terms of bioconcentration (where uptake exceeds elimination), and biomagnification (increased concentration via uptake from the food chain) (see Policy Definitions).

The persistence of any compound in the environment increases the chances of it bioaccumulating (as well as bioconcentrating and biomaginifying), especially if the compound has an affinity for a particular compartment in biological systems, e.g. it associates with fats, proteins or a particular organ [38,39,59,7]. Given that firefighting foams can be released to the environment under various circumstances, care must be taken to ensure that the behaviour of any potentially bioaccumulative compounds are well understood, especially those that are toxic and persistent.

Various long-chain fluorinated organic compounds are known to bioaccumulate and have been detected world-wide in various organisms [60,38,61]. Uptake of PFOS and PFOA is known to

occur for plants growing in contaminated soils and has also been found in food products including fish, meat and milk products [42].

Testing with aquatic species suggests that PFOA is "not highly bioaccumulative", however it should be taken into account that PFOA is highly soluble plus aquatic species used in standard tests have an additional mode of elimination via the large surface area of their gills that terrestrial animals do not have. That is to say, the gills are an added way that aquatic animals can more readily excrete contaminants from their bodies back into the water so tests using aquatic species should be viewed with caution in respect to their applicability to species without gills.

PFOA is also only one of a wide diversity of compounds that are used, occur in or are derived from foam, with very little being known about their behaviour in the environment [13,9,12]. Some compounds can persist for years to decades [62,63] before partially breaking down to end-point compounds such as PFOA and PFHxA.

It is worth noting that standard assessments of bioaccumulation potential using the N-octanol-water partitioning coefficient (K_{ow}) is not valid for surface active substances (surfactants) including fluorosurfactants as they do not tend to accumulate in storage lipids but rather associate with proteins and concentrate primarily in the blood and liver among other tissues [64,40,59,60,39].

Assessment of the bioaccumulative potential of substances against existing regulatory criteria for bioconcentration factors (BCFs) and bioaccumulation factors (BAFs), such as those developed under CEPA 1999, need to be applied cautiously and take into account that these threshold criteria may not be applicable as they are based on historical experience with neutral, non-metabolised organic substances in freshwater aquatic systems, with particular reference to lipophilic substances [41,11,59] which, unlike fluorinated organics, primarily partition into fats.

Fluorinated organic substances depart in their characteristics and behaviour from the traditional assumptions made regarding BCFs and BAFs in a number of significant respects, as well as there being indications of bioaccumulation occurring in a number of terrestrial and marine animals [65,41,38,20].

The unusual nature and behaviour of persistent toxic organic compounds, including per- and poly-fluorinated organics, strongly suggests that a conservative approach to management must be taken given that many show indications that they or their breakdown products may be bioaccumulative. For example, in earthworms (a primary trophic group) exposure to PFOS, PFOA and 6:2FtS gave similar bioaccumulation factors for PFOS (2.6) and 6:2FtS (2.4) suggesting undegraded 6:2FtS bioaccumulates to a similar extent as PFOS and PFOA [65].

2.7 Chronic (long-term) toxicity

Many comparisons have been made between the toxicity of fluorinated and fluorine-free foams. However, such comparisons are almost always in regards to short-term acute toxicity with rarely any mention of long-term chronic toxicity. When considering the potential adverse effects of toxicity the short-term toxicity characteristics of a product is only one aspect that should be considered and is not directly relatable to long-term toxicity.

Short-term toxicity is the most often cited characteristic in foam product information and SDS, it is misleading to assess and compare the potential effects of foams on this basis alone, especially when some products may contain persistent and bioaccumulative compounds with subtle, but nonetheless, toxic long-term effects in their formulation.

The long-term, chronic toxicity must also be considered in the light of how persistent the contaminants are in the environment, how they may be converted to other compounds and how they behave in biological systems. For persistent pollutants, such as fluorinated organic compounds, the degree of persistence is a very significant consideration in assessing the chronic toxicity risk posed to human health and the environment [66,33,61].

Put simply, persistent pollutants, even if they have relatively low acute or immediate toxicity effects, have a very long time over which they can exert their effects, especially if there are any

indications that bioaccumulation, bioconcentration and/or biomagnification could also occur or if there is slow elimination from the body [67,39,41].

2.8 PBT (Persistence-Bioaccumulation-Toxicity)

The overall potential for a firefighting foam to cause adverse environmental effects needs to be assessed in terms of its Persistence-Bioaccumulation-Toxicity (PBT) profile. This needs to take into account both the short-term and long-term impacts of the final formulation. Each component needs to be weighted appropriately in arriving at the overall evaluation.

Where there is insufficient information on a particular foam formulation, or the principle components of concern, a conservative approach to PBT assessment and product management needs to be taken in line with the *precautionary principle*. This is especially the case where there are compounds in use for which there are indications that long-term effects may be expressed through biopersistence, bioaccumulation, bioconcentration or biomagnification or where there is the potential for long-range transport and there are known occurrences of contaminants in biota that are very unlikely to be the result of direct exposure [20,41,68].

The general *persistence* of a compound refers to its overall persistence in the environment subject to degrading influences such as photolysis, oxidation, hydrolysis and biodegradation. The more specific terms *bio-persistence*, *bio-accumulation*, *bio-concentration* and *bio-magnification* refer to biotic processes within or involving living organisms.

The term *biopersistence* has been frequently misused in general publications and marketing information e.g. "*biopersistence* in the environment" has been used incorrectly where environmental persistence is more accurate and appropriate. Biopersistence specifically refers to

how long a compound, once taken up by the organism, persists in the body of the organism. This largely depends on the rate that it is cleared or eliminated [26,33] e.g. by respiration, excretion or metabolism (bioelimination). Bioelimination rates and mechanisms vary widely between organisms and may also be subject to sex-specific hormonally controlled differences within species.

When assessing the potential for adverse effects by bioaccumulation of the components of a complex mixture such as a foam concentrate factors that need to be taken into account include:

- Particular compounds that may bioaccumulate or are similar to those that are known to.
- Breakdown products or metabolites if they are similar substances or have similar effects.
- Solvents and detergents present in formulations that affect cellular uptake and metabolism.

While it is important to assess the effects of the combined formulation of any product, for practical purposes

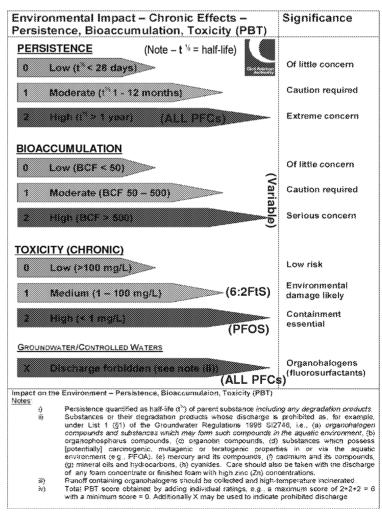


Figure 2.8 A - PBT simplified assessment [26]

an initial assessment of bioaccumulation potential can be focussed on the compounds most likely to be involved (and their breakdown products) that are significantly environmentally persistent. That is, all those compounds that persist long enough to bioaccumulate and could exert adverse effects on health and/or the environment. This might include fluorotelomers, fluoropolymers, siloxanes [69], metal ligands or similar compounds and their breakdown products.

Given that the formulations of firefighting foams are by commercial necessity trade secrets, this puts the onus on the manufacturers to review the compounds in their formulations, including all possible breakdown products, and provide the relevant information to the user even if the compounds are only identified in a generic way in SDS and product information, e.g. "Contains fluorinated organic compounds known to persist in the environment and are suspected to bioaccumulate in living organisms – Do not discharge to the environment".

The octanol-water partition coefficient $log(P_{ow})$ can in some cases be used to estimate the bioconcentration factor of a compound but this is not appropriate for surfactants [40,59] so a more direct measure of the bio-concentration factor (BCF) will need to be done [26].

In general, the potential for bioaccumulation (and bio-magnification) should be assumed as many poly- and perfluorinated organic compounds belong to a class of substances known to have a potential to accumulate in living organisms, there are indications from structural features and there is no mitigating property such as hydrolysis (half-life less than 12 hours) [70]. Individual BCFs for aquatic organisms are in any case only part of the overall trophic bio-magnification that can occur in food-chain, especially in higher predators [26].

The PBT profiling system proposed by the Civil Aviation Authority (Figure 2.8 A) provides a sound basis for a simplified PBT assessment in keeping with the precautionary principle mentioned elsewhere in these *Explanatory Notes*. For complex products this may need to be informed by a more detailed risk assessment similar to the Hazard Index method [37].

2.9 Health, safety, amenity and economic considerations

While the Management of Firefighting Foam Policy focusses primarily on the actual and potential impacts of firefighting foam on environmental values, questions have arisen regarding the potential health impacts of releases on the public, workers, firefighters and other responders as well as the broader effects on public amenity values, reputation, economic resources and costs to industry.

Since their first development and use fluorinated organic compounds are now found widely in the environment, plants, animals and the human population [5,41,71]. All foams contain a mix of various compounds in their formulations, often unique in the combination for each foam.

Common environmental effects of all foams are varying degrees of detergent toxicity and elevated biochemical oxygen demand that can have immediate adverse effects on biota in the aquatic environment. Further to that, some foams may contain compounds that can have long-term effects on worker health, public health, the environment and other values. Of particular concern are toxic compounds that are persistent, bioaccumulative and with long elimination times from animal species including the human body [72,73,39,67,62].

There is very significant evidence for adverse effects in mammals for many classes of fluorinated organic compounds and indications of similar problems for most others. The elimination half-lives for a range of fluorinated organic sulfonate and carboxylate compounds are variable across different mammals but are particularly long in humans [38,73,39,67,8,74] with elimination half-lives ranging from 1.5 years to 21.7 years (Table 2.9 A).

In the context of a person receiving a significant dose of PFOS (C8 compound) or PFHxS (notionally a C6 short-chain PFC, but behaving like a long-chain PFC), a number of half-lives may be required to reduce the concentration of the compound in their body to acceptable levels below which acute or chronic effects could occur; this may amount to a period of several decades.

This emphasises that it is all the more important the need to prevent significant exposure by responders and the public in the first place.

Table 2.9 A - Elimination half-lives in humans of PFHxA, PFOA and PFOS				
Compound	Half life	Perfluorohexane sulfonate		
C6, PFHxS	8.5 years (2.2 to 27 years)			
C8, PFOA	3.8 years (1.5 to 9.1 years)			
C8, PFOS	5.4 years (2.4 to 21.7 years)			
(PFHxS – Perfluoro	hexane sulfonate, C ₆ F ₁₃ O ₃ S, structure at right)			

2.9.1 The costs of incidents involving firefighting foam

Generally the focus on risk management for firefighting is on the immediate priorities of rapid and effective suppression or extinguishment of fire. In addition to this there needs to be consideration of the practicalities and costs of the recovery phase. Wherever possible there should be preplanning that seeks to minimise the unnecessary costs and impacts of the incident response.

Incidents often generate very large quantities of contaminated soil and firewater, and the cost of treatment can be significant under some circumstances and the damage to adjacent values beyond the site also being considerable. There are very limited options for treatment of wastewater and soils contaminated with persistent contaminants and most are expensive as materials have to be transported to treatment facilities and subjected to high temperature destruction methods such as incineration in a cement kiln [54,75,76,55,53,14] or subjected to chemical immobilisation.

The determination of overall risk is based on *Probability* X *Consequence (AS/NZS 31000:2009 Risk Management—Principles and guidelines)*. While the probability of a large-scale incident resulting in a significant release is relatively low, the lasting consequences when it does occur can be catastrophic with few options available during the emergency to control or prevent releases beyond the site that could result in impacts.

For example, the 2005 fire at the relatively small Buncefield bulk hydrocarbon storage facility in the UK necessitated the use of about 750,000 litres of fluorinated foam concentrate during the response. The incident generated about 55 million litres of firewater, most of which was released to the environment (just 16ML was recovered) with groundwater drinking water supplies for north London also compromised [77].

At Coode Island in Melbourne in 1991 about 200 tonnes of firefighting foam concentrate were used [78] on a dock-side hydrocarbon chemical storage facility fire and most of the firewater was released to the adjacent waterway. The foam used was probably 3M Light Water AFFF. Based on the two most likely formulations the release of fluorinated organic compounds is likely to have been very substantial at between 3 tonnes and 15 tonnes (Table 2.9.1 A).

This represents a release during the Coode Island fire of up to about 30,000 kilograms of fluorinated organic compounds about a third of which was PFOS [15]. The potential for significant effects on the environment, health of responders and the public from the perspective of the foam chemicals released was not recognised at the time and was not investigated.

Table 2.9.1 A – Coode Island fire, FOCs released based on 200 tonnes of concentrate used					
Foam type	3M Light Water FC-203 CE (1991)	3M Light Water FC-203 FC			
Composition from MSDS	alkyl sulfate salts 5%, amphoteric fluoroalkylamide derivatives 5%, perfluoroalkly sulfonate salts 5%	amphoteric fluoroalkylamide 1–5%, residual fluorochemicals <1%, PFOS salts 0.5-1.5%			
Fluorinated organic compounds	30,000 kg (PFOS 10,000 kg)	3,000 kg to 15,000 kg (PFOS 1,000 kg to 3,000 kg)			

Any large-scale release would be on top of and exacerbate the existing chronic low-level but nonetheless cumulative releases to waterways from domestic sources, such as carpet and fabric cleaning, inappropriate fluorinated waste disposal, and leaching of contaminated soils.

Investigations of the longer-term fate of relatively small releases and spills of perfluorinated organic compounds, (Toronto 2000, 330-1,650 kg PFCs [63,79] and Amsterdam 2008, ~572 kg PFCs [80]), have found elevated levels of fluorinated organic compounds persisting for at least 15 years in the aquatic environment, especially in sediments and fish [8] highlighting the potential for spills to have longer-term effects on environmental and fisheries values with a significant health risk posed to the public consuming seafood.

Exposure concerns are not just limited to PFOS, PFOA and higher homologues but also concern the shorter-chain compounds such as PFHxS (perfluorohexane sulfonate) that have been found in humans and associated with consumption of contaminated drinking water and fish [8,74]. PFHxS is present in, or results from some current and proposed alternative "C6 or 6:2 fluorotelomer-based" firefighting foams, as well as from legacy PFOS foams as it is a homologue of PFOS present as a contaminant.

A large-scale release of contaminated firewater from a large hydrocarbon storage facility incident, a hydrocarbon shipping tanker fire or even cumulative smaller releases to waterways and the marine environment would potentially impact those values not only by direct contamination of seafood resources and aquaculture stocks but also by generating the *perception* of contamination which is very likely to severely affect public opinion and local and overseas market purchases of local seafood produce.

For example, Queensland hosts commercial fisheries to the *annual value* about \$436 million with aquaculture valued at \$103 million and recreational fisheries valued at about \$73 million [81]. In Moreton Bay alone, adjacent to Brisbane, the value of commercial and recreational fisheries to Queensland's economy is between \$44 million and \$54 million per year [82].

Various marine oil spills and port dredging activities over the last decade, involving less persistent, and even undefined contaminants, compared to those associated with some firefighting foams, are examples where strong public and industry concerns have been expressed regarding pollution impacts on economic, amenity, cultural and recreational values [83,84].

If the pollution included indefinitely persistent and well recognised pollutants, such as fluorinated organic compounds, the damage to that industry, and to the recreational fishing sector and the state's reputation through actual or perceived contamination, might then extend for years to decades raising issues of who would be responsible for compensation for that period.

Where a large-scale incident involved non-persistent, biodegradable contaminants including organohalogen-free foam and hydrocarbons the extent of damage would be limited to largely acceptable short-term acute impacts from which the environment and resource values would recover with no risk of long-term harm or the perception of persistent pollution.

2.9.2 Human health and safety implications

While the very valid issues of responder and firefighter safety are recognised as a high priority in assessing the effectiveness of firefighting foam to provide protection against immediate threats during incidents the long-term health and safety aspects of exposure by users also need to be seriously considered as well.

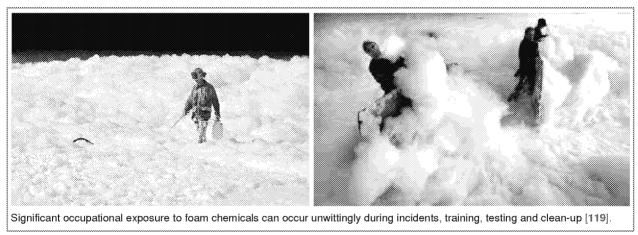
Subject to type, concentration, duration and frequency of exposure, some foam chemicals may represent a significant health risk for users who do not take appropriate personal protective measures such as wearing of respiratory protection against inhalation and ingestion of contaminants in aerosols [85]. For example, fine, easily dispersed and inhaled aerosol particles are well known to be produced by bursting bubbles. Oral (and by inference respiratory) PFOS and PFOA exposures are readily absorbed (90%) and distributed through the body in blood serum. Excretion pathways, such as in bile, can be confounded by reabsorption, such as in the gastrointestinal tract [8].

Various fluorinated organic compounds are present in the blood of the general human population of which PFOA and PFOS are the most frequently detected compounds and of significant concern for human health [48,86,74]. However, the prominence of PFOS and PFOA as research subjects may be a biased perception as other less well-known compounds have not been as widely researched and reported and probably many more remain to be unidentified [17,15]. PFOA and PFOS both have long residence times in human blood of more than 1,000 days [60] and other compounds may behave similarly. None of these fluorochemicals were detectable as organic fluorine in reference databank human serum samples taken before fluorochemicals were manufactured and used commercially shortly after World War II [87].

High levels of PFOS and PFOA are toxic for reproduction and development of the foetus and are potentially carcinogenic in animal tests [8]. In addition, 8:2 fluorotelomer phosphate diesters, 8:2 fluorotelomer alcohols, and PFOA show endocrine effects in different in-vitro and in-vivo tests. PFOA and PFOS are also associated with reduced humoral immune response in early childhood immunizations [60,8].

Probable associations have been found between exposure to PFOA, PFOS and other fluorinated organic compounds and health effects in humans including hyperuricemia, high cholesterol (hypercholesteremia), ulcerative colitis, thyroid diseases, testicular cancer, delayed puberty, asthma, kidney cancer, liver damage, preeclampsia, ADHD (attention deficit hyperactivity disorder), endocrine disruption and elevated blood pressure during pregnancy [60,67,8,73,88,74].

For occupationally exposed users the clear correlations with possible adverse health effects, biotransformation in the body, long body-residence times and lack of definitive information on the behaviour and un-researched effects of the diversity of (largely unknown) compounds and combinations mean that special care needs to be taken to prevent exposure to fluorinated organic compounds as part of day-to-day operations as well as during incidents where responders or workers unfamiliar with the issue may be unwittingly exposed.



For example, ingestion and inhalation of aerosols created by sprays, wind, heated vapours and bursting bubbles can result in direct contaminant intake including foam chemicals.

3 Treatment and disposal of wastes

Firewater that contains firefighting foam requires appropriate treatment and disposal based on its composition. The comments below refer to treatment and disposal firewater or wastewater that only contains firefighting foam. Any firewater or wastewater that contains other contaminants such as hydrocarbons, chemicals or products of combustion from a spill or incident needs to be considered in terms of the particular combination of contaminants as well as the firefighting foam content.

All solid and liquid wastes that contain fluorinated organic compounds (e.g. concentrates, firewater, wash-water, run-off, soils, absorbents, etc.) are regarded as regulated wastes and must only be disposed of through a facility that is licensed to take regulated wastes.

3.1 Firewater and wastewater treatment

Firefighting foams that are fully biodegradable can be treated and disposed of by wastewater treatment such as on-site treatment plant, degradation in holding ponds, irrigation to suitable land for degradation or by discharge to sewer for treatment at a municipal sewage treatment plant.

Appropriate consideration must be given to what site and system/method are to be used for treatment and/or disposal of fully biodegradable foam and that it is appropriate for that purpose and does not have a potential for releases that might cause environmental harm.

Discharges of foam, firewater or wastewater to sewer for treatment and disposal must be by permit or agreement with the authority accepting the discharge of the waste to sewer for treatment. Firefighting foams, wastewater or firewater containing significant levels of fluorinated organic compounds (see *Policy Section 6.4.2*) or similar persistent toxic compounds cannot be treated or removed by standard wastewater treatment processes but must not be discharged to sewer, it must be disposed of to a facility approved to treat such wastes. Fluorinated organic compounds are not captured by standard wastewater treatment processes [89,61.62].

Foams that contain any persistent toxic compounds, including fluorinated organic compounds, are not regarded as fully biodegradable for the purposes of the Policy and special consideration needs to be given to the potential for impacts associated with treatment and disposal of any persistent toxic compounds.

For firefighting foam containing persistent compounds such as fluorinated organic compounds the wastewater must be fully contained and not released to waterways or other bodies of water, stormwater, soils, groundwater or to sewer.

Municipal sewage treatment plants are not capable of treating or capturing fluorinated organic compounds such as PFOS, PFOA or the shorter-chain substitutes such as 6:2FtS [24,89,61,6] with the result that the fluorinated organic compounds are released to water bodies or land in their discharges as well as contaminating the sewage sludge or biosolids fraction that are subsequently sent to landfill or distributed for soil improvement i.e., agricultural "top dressing", leading to further leaching and release to the environment [42].

Waste managers accepting fluorinated organic compounds as concentrates, firewater, wastewater or in other wastes must ensure that they are fully contained and properly disposed of in such a way so as to completely immobilise or destroy them. Established methods for destruction include dedicated high temperature thermal incineration or in a cement kiln [54,75,76,55] where the fluorine component is ultimately captured by scrubbing of the flue gasses to remove hydrogen fluoride (HF) or immobilised in the cement matrix as inert and environmentally neutral calcium fluoride (CaF). Other forms of high temperature destruction such as in a plasma-arc furnace are equally effective. Such waste disposal facilities would need to be specifically licensed and appropriate conditions imposed for this type of activity in most jurisdictions.

Fixation of contaminated soils and solid materials with an appropriate immobilisation reagent may be feasible to the point where the wastes can be disposed of to a licensed landfill. Criteria to define what levels of contamination would require treatment and what levels of immobilisation/leachability for landfilling [90] would be acceptable are under consideration. Landfills (and WWTP) have been shown to be sources of small volatile fluorinated species capable of diffusing into the upper atmosphere with presumed global warming potential (GWP).

3.2 Foam concentrate disposal

Firefighting foam concentrates that are fully biodegradable can be treated and disposed of by a range of general waste disposal facilities subject to their relevant waste acceptance criteria.

Firefighting foam concentrates that contain persistent contaminants such as fluorinated organic compounds must be disposed of by methods that ensure their complete destruction or immobilisation [55,75,54]. Disposal by high temperature incineration using plasma-arc

destruction or injection into cement kiln processes is favoured for liquid wastes. Destruction in a cement kiln may also be feasible for contaminated soils or alternatively landfilling after fixation to immobilise all persistent organic pollutants.

3.3 Infrastructure contamination

Infrastructure such as pipework, rubber seals, flexible hoses, pumps, tanks, the floors of hangars and the surfaces of sealed fire-training pads that have been exposed to foam containing fluorinated organic compounds have been recognised as potentially significant and ongoing sources of contamination (e.g. of new infrastructure and stormwater) by fluorinated organic compounds from residues leaching out of such items.

For example, concrete and bitumen areas used for foam training have been found to retain fluorinated organics which are difficult to remove from their matrixes and may subsequently leach out of the surfaces and contaminate stormwater.

When carrying out maintenance, cleaning, decommissioning or replacement of such items the potential for short-term and long-term releases of residual contamination should be considered, risk assessments carried out regarding the potential for impact from low-level releases and mitigation measures adopted as appropriate.

4 Foam use issues

Firefighting foam is used across a diversity of industries that range from large-scale facilities to small mobile and hand-held applications. Each user group has to take into account the limitations imposed by their particular operational, health, safety, environmental and economic circumstances in choosing the type of foam and delivery systems that best meets their needs and obligations.

The following explanatory notes apply to the issues faced by some of these particular user groups in addition to the general considerations regarding the use of firefighting foam.

4.1 Fire brigades

Fire brigades are called on to deal with a range of large and small incidents involving various flammable solids and liquids. Accordingly they have on hand the types of firefighting foam that best suit the range of usual circumstances that require their use in industrial, urban and rural circumstances. Day-to-day fire brigade use of foam on spills and fires is sporadic and at unpredictable locations, most involving small-scale incidents such as at vehicle spills, industrial incidents and vegetation fires.

As a matter of course, each incident is assessed by the Incident Controller in terms of the scale of the incident and the potential for contaminants of any type to cause health impacts or environmental harm, whether from the foam in use or from spilled chemicals, fuels or fire residues, and to take any containment or clean-up measures that are necessary and practical.

When brigade appliances attend incidents at facilities where foam stocks and application systems are already present they have very little control over what type is available and how it will be applied and as a matter of course will use the foam stocks and systems present. If the Incident Controller has the opportunity, and it is safe to do so, it would be preferable to use fluorine-free foam stocks before using fluorinated foam where there is the potential for a release to the environment.

Where Fire Brigades are required to respond to a spill or fire at a facility that has existing firefighting foam and systems available on site it is the facility owner's or operator's responsibility to have:

- undertaken a proper risk assessment of the likely scale and impacts of an incident
- selected the most suitable foam for the risks and situation

- put in place containment measures as necessary
- made allowance for the potential involvement of fire brigade resources.

While Fire Brigades will endeavour to respond to an incident in the most effective way practical, the facility owner/operator is fully responsible for assessing the relevant risks on and off the site and for having in place the appropriate resources, measures, plans and procedures to control, contain and manage any releases to the environment of any contaminant. This includes having appropriate detailed response plans in place and having made appropriate choices about measures such as foam products, delivery systems and containment to achieve a best-practice standard for protection of life, health, environment and property.

Some industry operators are under the impression that once the Fire Brigade takes control of an incident that they are no longer responsible for the outcomes. That is not the case; the operator must have taken every reasonable and practicable measure to properly manage any foreseeable incident taking into account what scale and types of resources may be required to effectively deal with the worst-case incident.

Where fluorine-free firefighting foam is released to land, such as when used by an urban or rural fire brigade for ignition prevention, control, extinguishment, damping-down and training on vegetation fires, it is expected that no adverse effects will occur from the application of small amounts away from watercourses (e.g. less than ~500 litres of fully biodegradable, fluorine-free concentrate) across a wide area or fire front where all the foam will rapidly soak in and degrade in-situ. Significant releases directly to watercourses or other bodies of water should be avoided were possible.

Concentrated and repeated applications of fluorine-free foam, such as in areas where testing or training is carried out repeatedly onto a bare-earth area can result in the build-up of contaminants to the point where natural degradation is impeded by factors such as elevated concentrations of toxic components, depletion of oxygen and waterlogging. This raises the possibility of contaminants persisting long enough to be washed into adjacent watercourses or other water bodies by stormwater or to leach down to groundwater. In these situations there should be firewater control measures in place to prevent immediate releases to adjacent waterways or to any place that leads to such bodies of water and to assess whether groundwater is at risk.

Where firewater is generated, beyond that which can readily soak into the local soil to degrade, control measures such as bunding or ponds should be used to hold the water for at least 28 days to allow it to degrade before release and/or to evaporate.

Fire brigades should not have on hand or intend to use any firefighting foam containing fluorinated organic compounds that is intended for application on an area where it cannot be fully contained and the wastes appropriately collected and disposed of later. For example, roadside fuel spills or rural fire brigade use on bushfires.

4.2 Hydrocarbon refineries and large storage facilities

Fire protection measures at large hydrocarbon refineries and storage facilities are recognised as being of paramount importance to protect life, health, the environment and property. Many facilities are long-established with legacy-related restrictions such as their location adjacent to environmentally sensitive bodies of water, established roads and drainage layout, connections to third-party port facilities, limited space available for modification of operations and the difficulties in making changes to essential systems while continuing normal operations. This naturally places limits on their ability to make changes to procedures, systems and operations to keep pace with changing health, safety and environmental requirements.

Nevertheless changes need to be made over time to meet changing standards and obligations. It is recognised that for large industries significant planning and preparation needs to go into changes to essential systems associated with firefighting such as containment and control measures, delivery systems and foam type.

The emerging information regarding the previously unrecognised significant impacts of various aspects of firefighting foams on health and environmental values, as well as the occurrence of large-scale incidents such as the Buncefield (2005) and Coode Island (1991) fires, plus recent small-scale spills has culminated in the recent (but overdue) realisation that the risks of impacts from firefighting foam releases at all scales are no longer acceptable.

Hydrocarbon refineries and large storage facilities by their very nature require substantial fire protection systems with the attendant risk of the release of very large quantities of foam in contaminated firewater during incidents. This has the potential to have serious and long-lasting impacts on the adjacent areas, in particular in regards to damage to aquatic ecosystems that underpin a diversity of values such as ecological diversity, public amenity, recreational fishing, commercial fishing and aquaculture.

The legacy systems in place at existing large facilities almost certainly hold stock of foams such as fluoroprotein foams (FFFP) that are dependent on long-chain fluorotelomer (8:2Ft) PFOA precursor compounds for their effectiveness. These foams are not acceptable in the medium or long term as they effectively represent a potential release of PFOA to the environment (waterways, soils, groundwater, and atmosphere). In the meantime they must be fully contained in completely impervious bunding. Legacy systems may also contain or be contaminated with PFOS-containing foams.

4.3 Ports, shipping and offshore facilities

Fire protection measures for dock-side and on-water port facilities, oil and gas offshore exploration production facilities, and shipping face particular problems in being able to adequately protect life, health, the environment and property. As economic hubs for the transit of goods into and out of Australia it is essential to ensure that normal operation of facilities is not compromised and that any incidents are minimised in extent and duration.

Shipping, dock-side operations and oil and gas offshore exploration and production facilities present particular problems in regards to the release of any contaminants whether associated with wastes, chemicals, minerals, foodstuffs, hydrocarbons or firefighting foam. There are generally very limited opportunities to contain contaminants in large incidents that are not land-based, such as offshore facility fires and grounded ship casualties, plus the location of spills from shipping casualties is mostly unpredictable except that it can be assumed that an environmentally sensitive aquatic environment is almost always at risk with the potential for further dispersal of contaminants to other sensitive areas.

Regulations pertaining to systems and foam that off-shore facilities and international and domestic shipping are required to comply with and procedures to contain and deal with on-board firewater will have an effect as to what mitigation measures can be practically achieved and how much a facility, vessel or port operator may be able to influence how risks from incidents are managed. However, the Master of a vessel, the ship's owner, the vessel's insurer and the offshore facility operator are ultimately responsible for making good any damage that their vessel/facility cause in Australian waters and the port, shipping and/or offshore facility operator may have to deal with the ongoing effects of the incident.

Port, shipping and oil and gas exploration and production companies must demonstrate that their firefighting foam usage and firewater management meets ALARP environmental risk and best environmental practice.

A misconception that has arisen from time-to-time is the mistaken belief that foam used on a body of water can be contained and recovered in the same way as an oil spill by oil-recovery booms floating on the water surface. This is not the case, firefighting foams are *water soluble* and while there may be some foam bubbles floating on the water surface the vast majority of the foam becomes dissolved in the water column.

The key issue for port, shipping and offshore facility operators to consider in assessing what are suitable firefighting measures and foam types for their purposes is that foam is inevitably released directly to the aquatic environment, that is, directly to the ocean, river or estuary from

the dock-side fixed and portable systems, from the deck of the vessel, offshore platform and/or from response vessels such as firefighting tugs.

Where such a direct release to the aquatic environment is unavoidable the use of firefighting foams containing fluorinated organic compounds of any sort is not acceptable due to its persistence in the environment.

Only fully degradable foam that does not contain any persistent toxic compounds is acceptable for applications where there is a direct release to the aquatic environment. Short-term acute impacts, even if locally severe, are far preferable to the risk of long-term impacts that cannot be remediated with persistent toxic contaminants that contribute to the cumulative pollution load in the area or by dispersal further afield.

For all foams, including fluorine-free foams, there is a risk of short-term environmental impact from the acute toxicity of foam components such as the detergents and solvents as well as dissolved oxygen depletion impacts from BOD. In the case of shipping, port and offshore facility incidents the depth of water at the incident site is such that acute impacts from acute toxicity and BOD effects of non-persistent foam such as fluorine-free foam are unlikely to be significant given that dilution in the water column and dispersal by tidal flow will mitigate the risk of any immediate effects.

Any essential testing of systems for maintenance, safety proofing and certification purposes using foams that do not contain persistent toxic compounds is acceptable where the foam is fully biodegradable and releases are managed such that the risk of environmental harm is minimised.

4.4 Mobile plant and hand-held extinguishers

Mobile plant and hand-held extinguishers are relatively small-volume systems, generally only involving tens to hundreds of litres of dilute foam solution. Releases and wastes of this scale can usually be readily captured, cleaned up and disposed of.

Mobile plant, such as large mining vehicles, are required to have on-board systems for fire protection. These systems have specific specifications, certifications and other requirements including testing and maintenance at regular intervals. Given the mobility of the system and the relatively small volumes it is entirely practical for controlled releases to be properly contained and the wastes collected and disposed of appropriately.

The practice of releasing fluorinated foam wastes to the ground during discharge tests of mobile plant systems is not acceptable and a breach of environmental regulations. That is, it is a direct, wilful and entirely avoidable release to the environment of a variety of long-chain fluorinated compounds [13,12] that are known to be indefinitely-persistent and highly dispersible pollutants with the potential for health and environmental impacts though releases to bodies of water, groundwater, air or via contaminated soils and dust. They also represent a human health risk.

Foam wastes containing fluorinated organic compounds need to be collected, stored, transported and disposed of as regulated wastes with destruction by high temperature incineration or other acceptable means meeting regulatory requirements.

Similarly, biodegradable fluorine-free foams must not be released in a way that they are likely to cause environmental harm, such as by BOD impacts and acute toxicity effects if allowed to enter a body of water or groundwater. However, fully biodegradable foams with no persistent toxic contaminants may be able to be appropriately treated and disposed of on-site or at local waste treatment and disposal facilities. Unavoidable minor releases to ground are acceptable with no clean-up necessary provided that there is no significant potential for contaminants to affect bodies of water or groundwater.

5 Assessment standards and information

Significant challenges are faced by firefighting foam users, responders and regulators when managing the various aspects of firefighting foam use. This is hampered by the general lack of

current chemical, health and environmental information as well as the lack of defined standards for distribution of key elements. The Management of Firefighting Foam Policy sets out baseline requirements for basic testing and information disclosure on which assessments and decisions can be reasonably based.

5.1 Safety Data Sheets (SDS/MSDS)

Foam users, regulatory agencies and incident responders are heavily reliant on there being appropriate, relevant, comprehensive and accurate information available on which to base management and response decisions and planning.

The safety data sheet (SDS) is the most relevant and readily available document for these purposes with various chemical behaviours and characteristics routinely cited plus a dedicated section (Section 12) for information on environmental and ecological hazards.

Existing systems and requirements for SDS to be provided with products, understood by the user and held on site in a defined location are well established. This gives users and emergency responders the best chance for access when required in an emergency. All key information regarding ecological effects should be integrated in Section 12 of the SDS. Separate product brochures and supplementary information documents are rarely ever kept with the product SDS.

Given that firefighting foam can be applied at various different concentrations, intentionally or otherwise, the information in the SDS for firefighting foam must, where possible, be clearly expressed as being for the concentrate or product as sold. This may be supplemented by additional information on standard dilutions if that is considered operationally helpful.

To date significant problems have arisen for foam users, environmental regulators and incident responders in that information available in foam product documentation and in particular SDS have been very rarely adequate for environmental assessment purposes [3,17,32] with issues ranging across:

- SDS are out of date and no longer valid (>3 years old from publication date), for copies held on site as well as from some manufacturers/suppliers web sites.
- Very limited or a complete absence of relevant environmental information.
- Omission or non-disclosure of information on presence and effects of persistent compounds.
- Claims of biodegradability contradicted by the presence of highly persistent toxic compounds.
- Acute toxicity tests only reporting third-party test results for selected components and no
 tests carried out on the final foam formulation (i.e., no assessment of the overall synergistic
 effects of the components when combined in the formulation).
- Omission of information on toxic compounds such as preservatives and biocides.
- Failure to pass-on and disclose toxicity, persistence and hazard warnings provided by formulation component manufacturers.
- Non-relevance of the species used in toxicity tests.
- Non-standardised toxicity test periods (e.g. across SDS for 24, 48, 96 hours).
- Quoting of compliance with limited dangerous goods or other standards, worded so as to imply blanket compliance or approvals in other areas.
- Disingenuous statements that refer the user/responder to the "local EPA" as the authority for environmental impact information for a particular product where the "local EPA" will clearly not have any relevant information available for what are complex and usually "trade secret" formulations.

Some users, and even some regulators, have assumed that safety data sheets must meet an adequate standard in terms of information content, relevance and accuracy. Many are not aware that the SDS standard set by *EC Commission Directive 91/155/EC of 5th March 1991* is very broad in order to cover a vast range of substances and essentially only sets out the Sections that

need to be included in SDS. Traditionally SDS have been documents focussed on workplace health and safety issues, and then mostly focussed on short-term acute health impacts, with only relatively recent regard for the inclusion of even very basic environmental information [36].

The Australian National Industrial Chemicals Notification and Assessment Scheme (NICNAS) has similarly been focussed on SDS and label information content on health and safety issues associated with use and handling and on higher order obligations such as those under the *Stockholm Convention* [91].

The Foam Management Policy sets out the required minimum standards for test and composition information that must be made available so that users, regulators and incident responders can make reasonable assessment of the environmental risks. The level of information required is not such that proprietary formulations are at risk of disclosure, although there must be general and consistent disclosure of the presence of toxic and persistent components and impurities.

The minimum standards set also provide a common base for users to make appropriate comparisons, decisions and fair choices about what suits their application best when all performance, health, environment, regulatory and cost issues are considered. Manufacturers and suppliers may choose to enhance SDS content by providing additional relevant information and users may need to seek further information to address particular or unusual circumstances they face.

The inclusion of standardised, comprehensive, verified information in product information and SDS will also be of an advantage to manufacturers and suppliers as appropriate disclosure will give the user confidence as to whether or not the product is credible and fit for purpose against all their requirements and obligations.

5.1.1 SDS preparation

Manufacturers or importers of chemicals into Australia are responsible for providing an SDS that has been prepared in accordance with the Australian Workplace Health and Safety Regulations, and should check that any SDS prepared against overseas standards meets this.

The Safe Work Australia *Preparation of Safety Data Sheets for Hazardous Chemicals—Code of Practice (2011)* [36] provides guidance on the content that should be included in an SDS. A particular note is made in this Code that "While this Code applies to hazardous chemicals as defined, an SDS should be provided for any chemical that may adversely impact the health or safety of persons or the environment" and that the "SDS should reflect what is currently known about the chemical".

Guidance on content for SDS is constrained by the fact that SDS have to cover a very wide diversity of chemicals and substances across many industries and many jurisdictions, so there has been heavy reliance on the manufacturer to determine what is relevant content. Inevitably there have been inconsistencies and highly variable quality-of-information across manufacturers, even for products put to very similar uses and of similar composition.

5.1.2 Ecological information (SDS Section 12)

Section 12 – Ecological Information of SDS is the most relevant section that should contain comprehensive and relevant information about environmental effects. However, the information from many other sections on the product characteristics and behaviour will also be highly relevant and should also be considered when assessing the potential for adverse impacts on environmental values.

These Explanatory Notes and the Management of Firefighting Foam Policy provide clarification of what the basic content of at least Section 12 (and possibly other sections) of the SDS should cover and the issues that should be considered in risk assessment and decision making for management of foam.

There is very little coordinated, independent quality control on the accuracy and relevance of SDS content, especially in regards to environmental effects and SDS for firefighting foam suffer

from a significant lack of disclosure of key information that would be readily available or could be easily determined [17,15,16]. Given that the end-user ultimately assumes the liability for any product's use and its effects, it is also the user's responsibility to seek any further information regarding the product's fitness for purpose or any adverse effects it may have on health or the environment.

For users to be reasonably expected to assess their potential risks/benefits and liabilities for health, user safety and the environment, make informed choices about products and put into place associated controls, plans and measures to address health, safety and environmental issues, there needs to be more comprehensive and standardised information made readily available in product information and safety data sheets produced by suppliers.

The manufacturer or producer has responsibility for each of their products; after all they are the only ones who have knowledge of exactly what went into each of their products. The testing required by the Policy is not onerous and only needs to be carried out once for each formulation. This is no different to other certifications such as testing for firefighting performance for each formulation.

The end-user is not expected to undertake or duplicate the testing required by the Policy, as has been erroneously suggested to some users. However, the end user is ultimately responsible for seeking complete and appropriate information in regards to the suitability, performance and any health and environmental effects of the product(s) they consider or use.

A good guide to general SDS content and interpretation with coverage and explanation of all the essential elements of the sections including *Section 12 – Ecological Information* has been adopted by ExxonMobil for their products in their 2011 *User's Guide to Safety Data Sheets* [92]. This guide takes into account changes resulting from both *REACH Regulation (EC) № 1907/2006* as well as the *Classification, Labelling & Packaging (CLP) Regulation (EC) No 1272/2008* that implements the Globally Harmonized System in Europe.

Complementary to the *ExxonMobil Guide* is the 2012 *REACH and Safety Data Sheets* information leaflet [93] published by the UK Environment Agency as the REACH Competent National Authority which outlines the content and provision requirements for SDS.

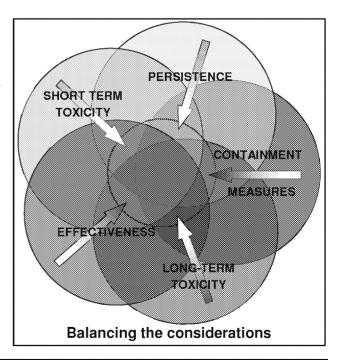
To address their responsibilities and liability, and to ensure that there is no misunderstanding about products put into service, end-users would be prudent to ensure that they seek and receive written confirmation of any information provided to them that is additional to that in the published SDS and product information.

6 Balancing considerations

Firefighting foams are a valuable and essential tool for protection of life, environment and property and incidents ranging from minor spills and fires to major incidents will continue to necessitate their use on land and at sea

As has been pointed out in submissions, and in large part is the main purpose of the Policy, the risks associated with firefighting foam use must be considered proactively, well before foam is put into service. This is especially important considering that during an incident the Incident Controller will have very few options open to them and very little time in which to consider them.

The Management of Firefighting Foam Policy recognises that a prime consideration when choosing and procuring firefighting foam is the



effectiveness of the foam for the intended firefighting application in providing adequate levels of performance, safety and property protection.

The system and foam options available that meet the appropriate performance standards and the user's operational needs must also be assessed in terms of a net environmental benefit analysis [94] to select the optimal combination amongst the available options that best addresses <u>all</u> requirements or fitness for purpose [3], including the relevant environmental protection standards.

All firefighting foams have the potential to cause adverse health and environmental impacts and must be managed proactively. The potential for releases, and therefore impacts, has been shown to be not only from their infrequent large-scale use on incidents but also through less obvious areas where there are less noticeable but more frequent releases.

The risks of impacts from releases range across:

- Large-scale, high-profile, very infrequent incidents where large amounts of contaminants of various type are usually released.
- Accidental spills, servicing, testing and training activities where moderate amounts of contaminants are released.
- Small scale spills from accidental spills and poorly managed maintenance and testing activities.
- Improper waste disposal through systems incapable of capturing and destroying contaminants, e.g. processing fluorinated foam wastes from fires or testing through wastewater treatment systems incapable of capturing fluorinated organic contaminants [89,61,62].

6.1 Large-scale release risks

Large-scale incidents such as the 2005 Buncefield hydrocarbon storage fire in the UK [77,95] are fortunately infrequent, however there are a range of smaller-scale incident that go unrecognised and unreported that contribute to the cumulative effects of some foams. During the Buncefield incident 750 tonnes of fluorinated foam concentrate was used (including significant quantities of PFOS) with about 12 megalitres (of a total of 16 megalitres) firewater still remaining to be disposed of. About the same amount was released to the environment which also resulted in part of north London's groundwater drinking water supplies being compromised.

A large release of firefighting foam from a large fuel terminal, port facility or shipping incident, for example, in or adjacent to Queensland coastal waters (similar to the Coode Island incident at the Port of Melbourne in 1991 [96], involving about 200 tonnes of foam concentrate [78]), would, depending on location, have the potential to impact on a significant part of Queensland's \$436 million per annum fisheries and aquaculture sectors [81] through contamination (or perceived contamination) of seafood and loss of local and overseas markets/reputation for quality.

By comparison, a large-scale incident involving foams formulated with non-persistent, fully-biodegradable compounds would be in-the-main self-remediating over a relatively short time with only short-term acute toxicity effects. In such cases the main focus would be on the impacts of the other contaminants and combustion products from the incident.

6.2 Small-scale releases

The potential for large-scale, but very infrequent, incidents tends to dominate discussions and considerations of risks while the less obvious chronic release categories are largely ignored. This is despite small-scale spills and fires, servicing, testing, training, maintenance and spills being common [65,45,17,79] and contributing very significantly to the risk of adverse impacts in the long term from poorly managed and generally unnecessary releases.

Recent examples of significant cumulative impacts include a rising number of cases of spills and legacy contamination from airport firefighting training areas contaminating surface and groundwater values. The Army Aviation Centre at Oakey is a current example where it has been

found that a plume of groundwater contaminated by PFOS over a long period extends several kilometres down-gradient from the source fire training ground with impacts on significant numbers of domestic and agricultural users accessing water from bore holes in that area [97].

The risk of impacts from the smaller, more frequent releases is exacerbated by lack of information available to the end-user against which they can assess the risks for their particular situation and make informed decisions about appropriate management measures they should have in place.

6.3 Considering the choices

Users need to carefully consider what combination of foam type, application systems and containment measures are best for their application and location. Achieving that balance requires consideration of a range of competing and sometimes opposing factors. What was previously an acceptable balance may change over time so needs to be factored in to choices and planning for continuous improvement to systems in the longer term.

For example, PFOS has been an exemplary compound for firefighting for some types of fires but its serious adverse impacts on health and the environment mean that it has not been acceptable in formulations for some time. Despite the widely available knowledge of the high risks attaching to PFOS industry users have failed to move to address the issue without regulatory intervention. Similarly PFOA and PFOA precursor compounds are being found to carry unacceptable health and environmental risks and most jurisdictions recognise that moves to phase out their use must occur as soon as practicable.

The lessons from the use of these and similar compounds have reinforced the need to apply the *precautionary principle* in the management of potential releases of contaminants, not only when adverse effects have become plain, but also when there are indications of such effects and there is insufficient information available to make a reasonable and informed assessment. It is irresponsible to release chemicals into the environment that will cause irreversible, planetary contamination unless it has been established that such chemicals are benign to the environment and human health [29].

Put simply, the *Absence-of-Evidence* for an adverse effect is not *Evidence-of-Absence*. In the case of fluorinated organic substances there is now more than adequate evidence and indications that our use of products containing any such compounds should be very cautious as the releases are unrecoverable, undegradable and the adverse effects may be substantial, permanent and ongoing. From a regulatory standpoint the *precautionary principle* must apply with the onus on the user/proponent to demonstrate conclusively that no adverse effects can

Accordingly if new generation shorter-chain C6-based fluorinated foam products are to be used there needs to be careful control of in terms of their purity and management as the information on their properties and effects is very limited [98,71,29] with significant indications that the *per-* and *poly-*fluorinated compounds with various functional groups (as well as fluoropolymers) share properties and effects with the fluorinated organic compounds already of serious concern.

Where feedstock chemicals used in the production of foam formulations state that the feedstock materials have characteristics such as "Toxic to aquatic life with long lasting effects", "Toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment", or that some information is not available for key attributes such as PBT/vPvB assessment, this information must be disclosed as a matter of course in the final product SDS so that end-users, responders and regulators can make informed assessments and decisions.

For the end-user of firefighting foams to make informed and soundly based risk assessments and decisions they need quality information and advice to include in their considerations as to what constitutes the best-practice combination of product, systems, procedures, containment measures and response planning that can best meet their various operational needs, regulatory obligations, health and safety standards, community expectations and economic goals.

7 Use of persistent organic compounds

Fluorinated organic compounds are the largest group of persistent organic compounds known to be very widely used in firefighting foam formulations, as well as in a wide range of other consumer products and industrial processes. Other compounds, such as siloxanes, may also be environmentally persistent depending on the specific compounds in use, therefore care must be taken to evaluate their effects and fate in the environment before they are put into widespread use.

The major concerns with fluorinated organic compounds after they are released to the environment include:

- diverse variety of compounds in use with little information on potential impacts of each
- permanent pollutants with indefinite environmental persistence
- · known to have various toxic effects on health and the environment
- · variously bioaccumulate in plants, animals and humans
- persist in the human body for a very long time (slow elimination)
- · can be transported over long distances by the air, oceans, waterways and groundwater
- end-products will continue to circulate in the environment undegraded
- toxic effects may be cumulative and exerted over an extended period of time
- populations and environments far away from the point of release may be affected
- adverse impacts on environmental, heath, amenity and economic values may be irreversible.

Considerable world-wide health and environmental concerns have been expressed generally in a wide range of published papers and by regulatory agencies regarding the use of fluorinated organic compounds and the lack of information on production volumes, uses, properties and biological effects of existing and fluorinated alternative compounds.

7.1 World-wide concerns

In addition to the general concerns expressed regarding fluorinated organic compounds there have also been specific statements issued voicing the concerns of groups of eminent scientific experts who work on the characterization, properties, analysis, environmental distribution and adverse effects of poly- and perfluorinated alkyl substances (PFASs). This includes the recent Helsingør Statement [71] and The Madrid Statement [98] which specifically raise issues directed at informing and cautioning regulators, manufacturers, distributors and end-users including:

- The world-wide occurrence of PFASs in humans, wildlife and the environment.
- The lack of decline in the occurrence of some long-chain PFASs despite regulatory controls.
- The very limited knowledge on the properties and effects of PFAS fluorinated alternatives.
- The wide range of adverse health and environmental effects attributed to PFASs.
- Less efficient fluorinated alternatives may lead to increased use, emissions, and exposure.
- Concerns about low testing requirements for mixtures of substances.
- The need for world-wide regulation of production and use of PFASs of all types.
- The persistence of alternative PFASs and their transformation products.
- Increased exposure to alternative PFASs implies increased risk of unknown adverse effects.
- The lack of toxicological data on PFASs from manufacturers.
- The limited technical capacity to destroy PFAS wastes world-wide.
- The need for tighter regulation and controls on PFAS-based products.
- Greater transparency by manufacturers on PFAS product content and potential effects.
- Ceasing use of PFAS-based products where a safer alternative exists.
- The need to develop non-persistent, non-toxic alternatives to PFASs.

The publication of these statements are a very strong indication of the high level of concern amongst a wide diversity of professional scientists eminently qualified to comment on the use and release of persistent organic pollutants based on current facts and indications of the behaviour, fate and adverse impacts on human health and the environment of these compounds.

7.2 Ongoing use of fluorinated compounds

Firefighting foam formulations that use fluorinated organic compounds are very diverse in their (largely unknown) formulations. The *Management of Firefighting Foam Policy* does not preclude the use of all fluorinated firefighting foams, however, there are restrictions on the purity of fluorinated compounds that can be used and the measures that must be in place to contain and manage releases. This is in line with the general intent of the *U.S. EPA PFOA Stewardship Program* which set the initial baseline principles and goals underpinning the direction to be taken for management of compounds of particular concern. This now needs to be extended in the light of the better understanding of fluorinated organic compounds that has emerged since then.

Significant difficulties in being able to assess the potential impacts of fluorinated firefighting foams arise from the "trade secret" nature of fluorinated firefighting foam formulations (acknowledged as a valid issue) as well as the general lack of relevant testing results for foams in their as-sold, final form meaning that there is a lack of information for users, responders and regulators with which to assess possible impacts.

The Policy does not require that detailed confidential formulations of any foam of a "trade secret" nature be divulged but rather that meaningful information is provided on key issues for each formulation marketed for use including:

- Acute and chronic impact test results for the final product as-sold (toxicity and BOD).
- Biodegradability that takes into account all the compounds used in formulations.
- Indications of persistence and bioaccumulation potential of compounds used in formulations.
- Classes and purity of fluorinated organic compounds where used in formulations.

Significant evidence and indications of the potential for adverse effects on human health and the environment by the wide range of both long-chain and short-chain fluorinated organic compounds used in firefighting foam are common including:

- All fluorinated organic compounds used in foams are extremely persistent or partially degrade to extremely persistent compounds including both long-chain and short-chain compounds.
- All fluorinated organic compounds are toxic to varying degrees to human health and the environment.
- Adverse effects have been found or indicated in animals, children and adults including developmental toxicity, neonatal mortality, carcinogenicity, kidney and liver toxicity, immunotoxicity and reproductive toxicity [74].
- Longer-chain fluorinated organic compounds have been shown to be bio-accumulative.
- Shorter-chain fluorinated organic compounds have shown potential for bioaccumulation [65].
- Shorter-chain fluorotelomer carboxylic acids are more acutely toxic than corresponding perfluorocarboxylic acids such as PFOA [67,99].
- Fluorinated organic compounds have been found to persist in the human body with long elimination half-lives for long-chain compounds and even longer for shorter-chain compounds (Table 9.2 A C8, 2.3 to 5.4 years, C6, PFHxS 8.5 years) increasing the potential for bioaccumulation in humans so that comparatively low exposures can result in large body burdens [38,74].
- Shorter-chain fluoroteleomers such as 6:2FtS persist and continue to concentrate in groundwater a decade after use has ceased at some sites [18].

As an example of fluorotelomer behaviour and persistence; The Tyndall Air Force Base (in the USA), which operated until 1992, used AFFF, (supplied ~1983-88), for firefighting training:

- Foam concentrate sample was found to have 12,000 ug/L 6:2FtTAS and 6,000 ug/L 8:2FtTAS (-thioamido sulfonates) with no 6:2FtS detectable in the concentrate.
- In 1999 groundwater samples from all four bore holes on site were found to have exceptionally high fluorotelomer sulfonate concentrations (6:2 & 8:2FtS >10,000 ug/L) [18].

These are assumed to have been derived from the partial degradation of the fluorotelomer thioamido sulfonates (X:Y-FtTAS) in the original foam concentrate.

 The fluorinated organic compounds in the groundwater samples consisted of 82% X:Y fluorotelomer sulfonates, 16% perfluoro sulfonates (probably mainly PFOS) and 2% perfluorocarboxylates (presumably PFOA and PFHxA).

This demonstrates:

- Production in the environment of 6:2FtS and 8:2FtS from thioamido sulfonate compounds.
- Persistence of the fluorotelomer sulfonates in the groundwater over a period of about 11 to 16 years (implying the need to consider X:Y-FtS compound effects over this extended period and not just the end-point compounds).
- Probably some production of PFOA and PFOS from precursor compounds.

Similar persistence of fluorotelomers in groundwater and soils is coming to light for a range of other facilities [63,79,80,97,18,100].

The effects of the various compounds on human health must also be considered not only in terms of exposure to the initial compounds but also in terms of the intermediate and end-point metabolic degradation products as the compounds interact within the various compartments and organs in biological systems [85].

This highlights the need to consider the potential for impacts to health and the environment in the short, medium and long term for fluorotelomers, intermediate partial degradation products and their end-point compounds. There is currently very little information available on the behaviour and effects of such compounds.

7.3 U.S. EPA PFOA Stewardship Program relevance

The U.S. EPA Stewardship Program which was put into place in 2006 [9,56,47] obtained commitments from eight global chemical companies to:

- By 2010 reduce product content of PFOA, higher homologues and precursors by 95%.
- By end of 2015 eliminate PFOA, higher homologues and precursors.

The Stewardship Program relates to production and new products and does not take into account that there are existing long shelf-life legacy stocks of products containing PFOS, PFOA, PFOA precursors, etc. still widely held that could be released. It also is not relevant to, and does not provide assurances about, products sourced from other countries and made by other companies that are not party to, or supportive of the Program.

The *U.S. EPA PFOA Stewardship Program* has provided some good initial direction relevant to fluorinated firefighting foam development and control in the U.S., and by inference other countries, but it is not comprehensive and consideration of the broader issues and information that has become available since its establishment in 2006 is required.

The OECD is expected to take over the *US EPA PFOA Stewardship Program* function and is considering how best to develop, facilitate and promote national and international product stewardship programmes and regulatory approaches for perfluorinated chemicals based on their existing work programmes and in association with other participating organizations of the IOMC [20].

The Management of Firefighting Foam Policy has taken into account a significant amount of more recent information that has emerged since the agreement in 2006 and bridges the gap between production-focused controls, production by companies who did not subscribe to the U.S. EPA PFOA Stewardship Program and the immediate risks associated with the continued use of legacy products by users not recognising the risks and voluntarily embracing the need for change.

For example, large stocks of PFOS foam are known to be still deployed potentially for immediate use in various systems on and adjacent waterways around Australia (and elsewhere) despite the current understanding of PFOS's adverse effects and its listing as a Persistent Organic Pollutant

under *Annex B* of the *Stockholm Convention* since 2009 [60]. An incident involving a one tonne spill of PFOS foam occurred in Queensland to a body of water connected to the *Great Barrier Reef Marine Park* in January 2013.

7.4 Long-chain fluorinated organic compounds

The OECD definition of long-chain fluorinated organic compounds refers to perfluoroalkyl <u>carboxylic acids</u> with seven or more perfluoroalkyl carbons (i.e., ≥7 perfluorinated carbons) and perfluoro-alkane <u>sulfonates</u> with six or more perfluoroalkyl carbons (i.e., ≥6 perfluorinated carbons) [60]. The "long-chain" definitions for carboxylates and sulfonates are different in number of C atoms because a sulfonate with a given number of carbons has a greater tendency to bioconcentrate and/or bioaccumulate than a carboxylic acid with the same number of C atoms and therefore behaves like a long-chain fluorinated organic compound.

Although the OECD 2011 definition does not include perfluoroalkyl substances other than carboxylates and sulfonates, other compounds, with functional groups such as betaines, amines, thioethers, etc., with a perfluoroalkyl chain ≥8 are similarly considered long-chain [9,56,60].

The carbon chain length is not the only factor influencing toxicity, mobility, bioaccumulation, etc. The type of compound (e.g. fluorotelomer alcohol, sulfonate, carboxylate, betaine, etc.) and whether all carbon atoms are fluorinated have a bearing and must be considered. For example, fluorotelomer carboxylic acids (FTCA) are generally more toxic by one to four orders of magnitude to aquatic organisms than the corresponding perfluorocarboxylic acids (PFCA) [34.99].

Many firefighting foams currently deployed still rely heavily for their effectiveness on long-chain fluorinated organic compounds (e.g. 8:2Ft, 10:2Ft) which are of significant concern for human health and the environment in themselves and because of their degradation products. This means that foams that contain PFOS, PFOA, their precursors and higher homologues need to be taken out of service as soon as practicable.

PFOS has been of particular concern for some time as a persistent organic pollutant under the *Stockholm Convention* and has well known adverse health and environmental effects. As a matter of priority PFOS foams must be taken out of service *as soon as possible* and must not be used. Many instances of PFOS foam still being in service in Australia are coming to light.

The European Union Commission Regulation (No. 757/2010) required that all foam containing PFOS above 10 mg/kg (0.001% w/w or 10 ppm) must not be used after 27 June 2011 and this was adopted by the UK Environment Agency in February 2011 [53,58]. Accordingly:

- The maximum allowable impurity for PFOS in any firefighting foams has been set in the Policy to 10 mg/kg.
- Foams that contain PFOS above 10 mg/kg impurity limits are of greatest concern and must be taken out of service as soon as possible and must not be used.

Canada prohibited the use of foam containing PFOS above 0.5 ppm (0.00005%) from 29 May 2013 [63,101] in Regulations that came into force on 29 May 2008. New Zealand also excluded PFOS and PFOA from use in any solid or liquid substances that are imported or manufactured for use as a fire fighting chemical in the *Fire Fighting Chemicals Group Standard 2006* under the NZ *Hazardous Substances and New Organisms Act 1996.*

Foams that contain PFOA, PFOA precursors and their higher homologues (including fluoropolymers) at overall concentrations above 50 mg/kg are of similar concern and must be taken out of service as soon as practicable and must not be used. Relevant to the practical implementation of this is:

- Stocks of PFOA-contaminated/PFOA-precursor containing foams are still in service and time is required to properly consider replacements.
- Changes to foam delivery systems may be necessary and timeframes for replacement are to be negotiated on a case-by-case basis.

- Agreed individual plans will be put into place detailing how and when changeover is to be achieved.
- All PFOA-contaminated/PFOA-precursor containing foams are to be out of service by no later than two years from the Policy being approved. This provides for a changeover period beyond the anticipated timeline for the elimination of PFOA and related compounds from products by the end of 2015.

7.5 Short-chain fluorinated organic compounds

Foams based on formulations using high-purity, short-chain (≤C6) fluorotelomers have been under development as alternatives to the more toxic, more bioaccumulative, longer-chain compounds. This is in line with the *U.S EPA PFOA Stewardship Program* goal of elimination of PFOA, PFOA precursors and higher homologues by the end of 2015.

While there has been progress in moving towards shorter-chain C6-based foams there are still many foams, some promoted as "predominantly C6", which still rely heavily on a significant proportion of long-chain compounds in their formulations (e.g. up to 75% C7-9, up to 32% C8-12) [13,12,20].

There are a wide diversity of compounds with six perfluorinated carbons that are used in foam formulations (Tables 2.1 A & B) with no doubt more to be reported, each with different characteristics and (largely unknown) effects. Six-carbon perfluorinated compounds (and shorter) are reported to be generally less toxic and less bioaccumulative than the longer-chain compounds and therefore have been considered as potential replacement compounds.

The development of C6-based foam formulations, initiated by the *US EPA PFOA Stewardship Program*, has been underway for some time (2006) and has provided the opportunity to transition away from foams based on long-chain C8 compounds (and their homologues) and to develop and assess C6 foams of potentially lower risk.

However there is still insufficient information publicly available to conduct realistic risk assessments with major gaps in information [16,74] with:

- Few indications of the proposed fluorinated alternatives with many probably still unidentified.
- For identified alternatives, information on their behaviour, fate and potential impacts on health and the environment is insufficient.
- Proposed volumes of fluorinated alternatives that might be used and released are unknown.

The use of new generation fluorinated foams that have in their formulations (or will have) shorter-chain fluorotelomers (e.g. 6:2 Ft) needs to be qualified as there still needs to be appropriate management as there are a range of concerns, some that have arisen or have been better elucidated since the 2006 *US EPA PFOA Stewardship Program* commenced.

Significant issues that need to be considered for short-chain fluorinated organic compounds include:

- End-point perfluorinated compounds produced by degradation have the same extreme persistence of all other perfluorinated organic compounds.
- The functional groups on the compounds strongly influence their properties (e.g. the differences between betaines, carboxylic acids and sulfonic acids in acidity (pKa), acute toxicity, bioaccumulation and bioelimination).
- The partial degradation/transformation steps, intermediate products, half-lives and environmental effects of fluorotelomers are poorly known [47]. For example, 6:2 fluorotelomer mercaptoalkylamido sulfonate (FTSAS), common in many AFFF, is regarded as a potential source of fluorotelomer sulfonates, fluorotelomer alcohols and fluorotelomer carboxylic acids [15]. Processes similar to the biotransformation of 6:2 FTOH may occur which involves nine intermediate products through 6:2 FTCA, PFHxA to PFBA [47].

- Many still show the same PBT characteristics of longer-chain compounds albeit at reduced levels [65,18] e.g. PFHxS (C6) is regarded as having the characteristics of a "long-chain" sulfonic acid [60] and PFHxA has higher ecotoxicity than PFOA to aquatic species [29].
- Short-term acute effects are largely unknown or unpublished.
- Long-term chronic effects are largely unknown [42,47,99].
- While in X:Y fluorotelomer form the compounds have at least an extra two carbons in the chain e.g. a 6:2Ft is eight carbons long until it partially degrades.
- Short-chain compounds are *not* non-toxic and not necessarily non-accumulative [65]. For example 6:2FtS exhibits similar levels of liver and reproductive toxicity to PFOS [37].
- Mobility in soils and water (and therefore dispersal) is generally higher for the shorter-chain compounds [6,60,42,29] with likely higher uptake into leaves, stems and fruits [29].
- Combinations of different fluorotelomers are used in foam formulations with little information available on their single or combined synergistic effects and those of their breakdown products [18].
- The breakdown product of many current C6 fluorotelomer-based foams is 6:2FtS [20] which is regarded as a "long-chain" and has a greater tendency to bioconcentrate and/or bioaccumulate than a PFCA with the same number of C atoms e.g. C6 PFHxA [9].

Potential degradation products from the new fluorotelomer products and raw materials include the 5:3 acid, PFPeA (perfluoropentanoate) and PFHxA (perfluorohexanoate), depending on environmental conditions [102]. A study of ski-wax technicians exposed to PFCs showed that the perfluorocarboxylic acids PFHpA, PFOA, PFNA, PFDA and PFUnDA all bioaccumulated, with PFHxA having a relatively short half-life in man compared to other perfluorocarboxylic acids [103].

Measurements made of groundwater concentrations at former US military firefighting foam training sites indicate that PFOS, PFOA and 6:2 FTS all have environmental half-lives of at least a decade, with some samples still foaming 10-15 years after the sites were last used [18]. Similarly in Norway 43 airports that had previously used fluorinated foams were investigated for PFC contamination [100] with PFOS, 6:2FtS and other PFCs found to be present in soils, surface water, groundwater and biota.

The *U.S. EPA PFOA Stewardship Program* and the agreements that were entered into by the major chemical companies do not provide any guidance on what the final quality targets are for the "*elimination of PFOA, PFOA precursors and higher homologue chemicals*" from products [104] in terms of allowable impurities although there has been some progress on understanding what is desirable and what is achievable. Clearly total 100% elimination with no traces of impurities whatever is not practical or measurable, so achievable targets need to be set and have been considered in the Policy.

As a benchmark for achieving the Stewardship Program goals DuPont has indicated in technical information (2008 & 2012) that its foam feedstock CapstoneTM products (1183, 1157 & 1157D) [105,106] meet the goals of the *US EPA 2010/2015 PFOA Stewardship Program* with a PFOA impurity target below LOD (limit of detection) where LOD is referenced to a method appropriate for PFOA, precursors and higher homologues [107] with a LOD in the range *sub ug/g and LOQ ug/g* (ug/g = mg/kg or ppm w/w). DuPont also indicated in 2009 that PFOA content in aqueous-based dispersions will be or have been reduced *to a level below 50 ppm* [108].

This limit is supported by 2010 industry estimates based on an assumption of less than 1 ppm PFOA impurity in AFFF having up to 0.5% fluorotelomer content [20] compared to older generation foams with 0.9% to 1.5% w/w of fluorinated organic compounds [44].

The foam Policy therefore considers a limit of 50 mg/kg for PFOA, PFOA precursors and higher homologues, as impurities in the foam concentrate, to be a reasonable and achievable standard for impurities in short-chain fluorotelomer-based foam formulations. The limit on PFOS is dealt with separately.

7.6 Alternatives to fluorinated compounds

The growing recognition of the environmental and health problems associated with fluorinated organic compounds has driven investigation of alternative fluorine-free and other non-halogenated compounds that may impart similar beneficial firefighting characteristics to firefighting foams, particularly those that may have the ability to form aqueous films, such as trisiloxane surfactants.

As with any new product the development phase must include close scrutiny of the potential adverse effects on health and the environment so as to avoid the past mistakes of putting into service unsuitable and damaging products.

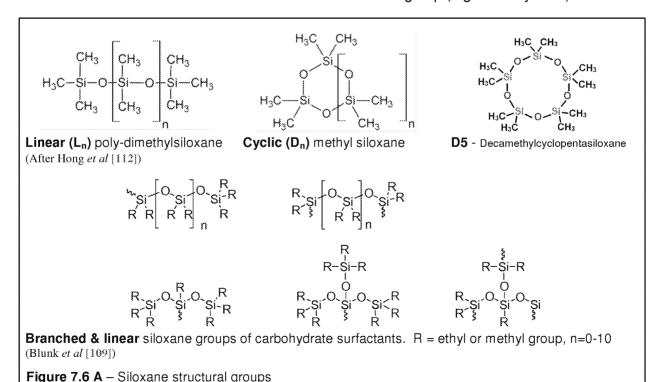
Siloxane surfactants have recently emerged as a promising alternative for formulation of halogenfree AFFF where the siloxane group in various carbohydrate siloxane compounds forms the hydrophobic part of the surfactant [109]. However, associated publications refer to "environmentally-sound high-performance siloxane surfactants" [110] and "environmentally friendly" [111] without any reference to, or elucidation of, the basis for stating that that the proposed surfactants are acceptable in terms of even the primary issues of persistence, biodegradability, BOD, COD, bioaccumulation or acute and chronic toxicity.

All foams have the potential to cause significant environmental harm, even if only through short-term detergent toxicity and BOD effects in water bodies, so none can be validly described as "green" or "environmentally friendly" as is sometimes used in promotional material.

The siloxane compounds most commonly in general use have been identified as variously being environmentally persistent, bioaccumulative, toxic, having the potential to cause health issues such as endocrine disruption, liver and lung injury and have the potential to cause ecological harm [112,113].

Siloxanes can be grouped into three structural groups (Figure 7.6 A) [112,109,114]:

- Cyclic siloxanes, having a closed-ring structure such as methyl siloxanes expressed as D_n where (n) is the number of silicon atoms in the ring (e.g. D₄, D₅ & D₆).
- Linear siloxanes compounds, expressed as L_n, having (n) silicon atoms in a chain-like structure (e.g L₄ - L₁₇)
- Branched and linear siloxanes attached to a functional group (e.g. carbohydrate).



Based on chemical principles, non-cyclic siloxanes with biodegradable functional groups such as carbohydrates may be biodegradable with low or limited persistence. However, this is not evident from the published papers that were reviewed as most research has focussed on cyclic methyl siloxanes (e.g. D_n siloxanes) which exhibit various adverse effects [112,115,114,116,117].

8 Use of non-persistent foams

Given the intense focus on the problems and risks identified with foams that use fluorinated organic compounds such as PFOS and PFOA in their formulations much discussion has been polarised in terms of "fluorinated" versus "fluorine-free".

While this polarisation may be valid in terms of the differences in the underlying firefighting mechanisms between the main foam types, the underlying issues from an environmental perspective, beyond the acute short-term toxicity and BOD effects applicable to all types of foam, are more correctly about the use and impacts of foams with:

- Persistent toxic compounds with potential to cause long-term adverse impacts.
- Non-persistent toxic compounds with short-term adverse environmental impacts.

It is quite conceivable that a fluorine-free, firefighting foam could have long-term adverse impacts from the inclusion of persistent compounds or persistent breakdown products which may be toxic.

For example, *cyclic* siloxanes (used extensively in personal-care products, e.g. D5 Decamethylcyclopentasiloxane in Figure 7.6 A), have been considered for use in firefighting foams but found to be ineffective and have environmental persistence, bioaccumulation and toxicity characteristics that make their release to the environment highly undesirable.

Accordingly the term *fluorine-free* foam is used interchangeably to also mean *non-persistent* foam.

All firefighting foams can have adverse environmental impacts. There is no foam that is completely environmentally benign. As is the case with fluorinated foams there are many diverse formulations of non-persistent, fluorine-free foams and all need to be assessed for firefighting effectiveness for the particular application as well as assessment for their potential environmental impacts against the relevant criteria. The primary environmental impact concerns for fluorine-free foams are their biochemical oxygen demand when released to bodies of water and groundwater and their short-term acute toxicity, primarily due to the synthetic detergents and solvents in their composition.

The general claim that has been circulating that "fluorine-free foams do not work" in terms of firefighting performance is disingenuous. The same high performance certification standards are applied to the testing for all foams regardless of their composition with rigorous tests carried out by independent certification organisations to the agreed standards. Foam must be selected according to the particular application. Many fluorine-free foams are acknowledged as "meeting the toughest amongst the firefighting standards" [20,118,23,109] and exceed film-forming fluorinated foam performance in various circumstances. Similarly the performance of AFFF is variable with some aqueous film forming foams (AFFF) failing to form aqueous films under some circumstances.

Even a brief review has found that various fluorine-free foams from a range of manufacturers meet the independent certifications for all the major firefighting applications including LAST Fire Test, EN1568(1-4), DEF(Aust)5706, ICAO Level B&C, AS5062 and reputedly US Mil Spec/UK Defence Spec in terms of performance but not in terms of the legacy requirement in Mil Spec to have a specified fluorine content (which may be under review).

Performance certification authorities that undertake these tests include MPA Dresden, CAAi UK, FM Approvals, Underwriters Laboratories Inc., SP Technical, Resource Protection International, SP Sweden and DNV Norway.

A cursory investigation of the extent of fluorine-free foam use around the world (with a focus on Australian use given the Policy relevance to Australia) found about 183 fire brigades, facilities and corporations that are using fluorine-free foams including at least:

- Airports 23 Australian (predominantly Air Services Australia), 54 overseas.
- Fire brigades 5 Australian, 19 overseas.
- Corporations 13 Australian, 34 overseas.
- Ports 12 Australian, overseas ports not investigated.
- Petroleum products 7 Australian, 13 overseas (including offshore oil and gas platforms).

At present hand-held foam-type fire extinguishers are the only extinguisher type where a fluorine-free foam has not yet been certified for use but development is reportedly underway for a fluorine-free foam to comply with AS1841. In the meantime it is eminently practical for the small amounts of fluorinated foam, contaminated materials and wastes produced in hand-held extinguisher incidents and servicing to be dealt with appropriately. This being implemented properly will largely depend on the supplier making the user aware (in Section 12 of the SDS and other documents) of their liability and the requirement for containment and clean-up of wastes containing persistent organic pollutants.

The general marketing claim that all fluorine-free foams are "10 times more toxic" (than fluorinated foam) is also without foundation, or at best is a claim that is out-of-date and refers only to acute short-term toxicity. A brief review of acute toxicity across foam types (where there is sufficient information to do so in SDS) finds similar relative toxicity and overlap in values such as LD50 and LC50 depending on manufacturer and foam type [26]. The potential health, safety and environmental effects of each foam need to be assessed in terms of not only their acute short-term toxicity (the most basic and often-quoted measure) but also the potential for long-term chronic toxicity effects, as well as environmental persistence, which have so far rarely been considered.

A further argument levelled against fluorine-free foams, again based on no consistent, verifiable evidence has been that so much more will need to be applied and more frequently in an incident. Even if it were to be necessary to use higher concentrations or larger amounts (on very infrequent events), the resulting short-term, but recoverable and naturally remediating damage is preferable to permanent pollution events that have no prospect for recovery or break down of persistent contaminants and represent a long-term threat to the environment.

In comparison to fluorine-free foam use, the proposed alternative pure C6 short-chain fluorinated compounds reportedly may require greater concentrations of the fluorinated organics in their formulas to achieve the same firefighting performance so it could be said that this may result in larger amounts of persistent organic contaminants being released than for legacy foams. This could therefore negate the lower (short-term) toxicity and bioaccumulation characteristics of the proposed alternative shorter-chain compounds and result in health and environmental exposures for compounds where little is known of their behaviour and effects [98,71].

9 Policy implementation

The General Environmental Duty (GED) under existing environmental legislation requires that any person, corporation or organisation carrying out an activity must take all reasonable and practicable measures to prevent or minimise the potential for the activity to cause environmental harm, having regard to the current state of technical knowledge for the activity and other relevant matters. Failure to comply with the GED obligations under the legislation could result in statutory action by the regulatory authority. Similarly knowingly causing environmental harm through the release of a pollutant is an offence that can result in statutory action by the regulatory authority.

Sites that carry out their activities under licences required by environmental legislation may also have additional specific obligations to comply with licence conditions regarding how they carry out the licensed activity and what they are permitted or not permitted to release to the environment.

All firefighting foams have the potential to cause environmental harm, particularly in bodies of water through impacts by BOD, acute toxicity, chronic toxicity and release of contaminants of serious concern, including highly persistent, toxic fluorinated organic compounds. All reasonable and practical steps must be taken to manage and mitigate that risk. For firefighting foams it is now becoming clearer what constitutes the current state-of-knowledge and best practice regarding the management options, risks and potential impacts.

The Managing Firefighting Foam Policy takes into consideration the current state-of-knowledge as of November 2014 (including recognition of the gaps in that knowledge) to set out what is currently considered the basic environmental considerations and standards that need to be met by the suppliers and users of firefighting foam so that the user (who carries the bulk of the liability and risk) can achieve best practice and meet their obligations.

The Policy review and drafting process has taken into account the various and often competing considerations that the user faces in achieving a balanced and practical solution amongst the options available with compromises expected in some areas. Consideration has also been given to what constitute essential and reasonable standards and timelines for users to meet the Policy requirements.

9.1 General compliance timelines

PFOS-containing foams (including foams containing PFOS precursors) represent a very significant risk to human health and the environment. Users must determine if they have PFOS foams and if so they must be taken out of service immediately and disposed of properly. Where the origin or type of foam is in any doubt the user must undertake testing to determine its general composition against the Policy standards and take action accordingly.

Foams containing long-chain fluorinated organic compounds such as PFOA, PFOA precursors and higher homologues must be replaced as soon as practicable with a fluorine-free or C6-compliant foam. While this is being implemented interim measures must be put in place as soon as possible to prevent releases of foam to the environment. Note that new generation pure C6 foams must be fully contained, must not be discharged to the environment (including bodies of water, soils or groundwater) and any wastes must be properly disposed of.

9.2 Up to two years for large facilities to comply

Where significant changes to systems are required to come into compliance with the Policy and environmental legislation a period of *up to a maximum of two years* from the date of approval of the Policy is considered reasonable to implement such changes. Such changes must be made without undue delay within that period and the facility must be able to demonstrate that they can contain all releases from day-to-day activities and incidents in existing systems or by effective interim measures.

If there are justifiable reasons why changes cannot be carried out within two years then the operator of the facility can submit a set plan for regulatory approval under the available provisions of the state environmental legislation.

References

- [1] National Fire Protection Association, "NFPA 11 Standard for Low-, Medium-, and High-Expansion Foam 2005 Edition," *NFPA Standards*, 2005.
- [2] EPA Victoria, "Demonstrating Best Practice," Guideline 1517, 2013.
- [3] Civil Aviation Authority (United Kingdom), "Comment Response Document Proposed Information Paper on Aviation Fire Fighting Foam," Aerodrome and Air Traffic Standards Division, London, 2013.
- [4] Marek Trojanowicz and Mariusz Koc, "Recent developments in methods for analysis of perfluorinated persistent pollutants." *Microchim Acta*, vol. 180, pp. 957–971, 2013.
- [5] U.S. Environmental Protection Agency, "Emerging Contaminants Perfluorooctane Sulfonate (PFOS) and Perfluorooctanoic Acid (PFOA)," *Solid Waste and Emergency Response fact Sheet EPA (5106P)*, vol. 505-F-14-001, March 2014.
- [6] Claudia Staude and Dr Annegret Biegel-Engler, "Per- and polyfluorinated Chemicals (PFC) Effects of foam extinguishing agents on the environment," Federal Environment Agency (Germany), ENVIRONMENTAL PROTECTION 4-2013, 2013.
- [7] Xinghui Xia, Andry H. Rabearisoa, Xiaoman Jiang, and Zhineng Dai, "Bioaccumulation of Perfluoroalkyl Substances by Daphnia magna in Water with Different Types and Concentrations of Protein," *Environmental Science and Technology*, vol. 47, p. 10955–10963, 2013.
- [8] Michigan Department of Community Health, "Technical Support Document for Assessment of Perfluorinated Chemicals and Selection of a Perfluoroctane Sulfonate (PFOS) Reference Dose as the basis for Michigan Fish Consumption Screening Values (FCSVs)," State of Michigan, Lansing, Michigan, Health Consultation 468766, 2014.
- [9] Robert C Buck et al., "Perfluoroalkyl and Polyfluoroalkyl Substances in the Environment: Terminology, Classification, and Origins," *Integrated Environmental Assessment and Management SETAC*, vol. 7, no. 4, pp. 513–541, 2011.
- [10] Yuichi Miyake et al., "Trace analysis of total fluorine in human blood using combustion ion chromatography for fluorine: A mass balance approach for the determination of known and unknown organofluorine compounds," *Journal of Chromatography A*, vol. 1154, pp. 214-221, 2007.
- [11] Mark J. Strynar, E. Laurence Libelo Andrew B. Lindstrom, "Polyfluorinated Compounds: Past, Present, and Future," *Environmental Science and Technology*, vol. 45, pp. 7954–796, 2011.
- [12] Benjamin J Place and Jennifer A. Field, "Identification of Novel Fluorochemicals in Aqueous Film-Forming Foams Used by the US Military," *Environmental Science and Technology*, vol. 46, p. 7120–7127, 2012.
- [13] Will J. Backe, Thomas C. Day, and Jennifer A. Field, "Zwitterionic, Cationic, and Anionic Fluorinated Chemicals in Aqueous Film Forming Foam Formulations and Groundwater from U.S.Military Bases by Nonaqueous Large-Volume Injection HPLC-MS/MS," *Environmental Science and Technology*, vol. 47, p. 5226–5234, 2013.
- [14] Norwegian Environment Agency Kine Martinsen, "Persistent Organic Pollutants Global and Local Impacts of Perfluorinated Compounds," in *ICCL-workshop, Durban 2013*, Durban, South Africa, 2013, pp. 1-15.
- [15] Barbara Weiner, Leo W. Y. Yeung, Erin B. Marchington, Lisa A. D'Agostino, and Scott A. Mabury, "Organic fluorine content in aqueous film forming foams (AFFFs) and biodegradation of the foam component 6:2 fluorotelomermercaptoalkylamido sulfonate (6:2 FTSAS)," *Environmental Chemistry*, vol. 10, pp. 486-493, 2013.
- [16] Zhanyun Wang, Ian T. Cousins, Martin Scheringer, and Konrad Hungerbühler, "Fluorinated alternatives to long-chain perfluoroalkyl carboxylic acids (PFCAs), perfluoroalkane sulfonic acids (PFSAs) and their potential precursors," *Environment International*, vol. 60, pp. 242-248, 2013.
- [17] Daniel Hirth, Sim Ooi, and Ruth Jarman (BlueSphere Environmental), "Investigation of Organic Fluorine in AFFF and Groundwater at a Fuel Storage Facility," in *Ecoforum 2014*, Gold Coast, Australia, 2014, pp. 1-27.

- [18] Melissa M. Schultz, Douglas F. Barofsky, and Jennifer A. Field, "Quantitative Determination of Fluorotelomer Sulfonates in Groundwater by LC MS/MS," *Environmental Science and Technology*, vol. 38, pp. 1828-1835, 2004.
- [19] Robert C. Buck, Peter M. Murphy, and Martial Pabon, "Chemistry, Properties, and Uses of Commercial Fluorinated Surfactants," in *Polyfluorinated Chemicals and Transformation Products*, Th.P. Knepper and F.T. Lange, Eds.: Springer, 2012, pp. 1-5.
- [20] RPS Advies B.V., Delft, The Netherlands, "Analysis of the risks arising from the industrial use of Perfuorooctanoic acid (PFOA) and Ammonium Perfluorooctanoate (APFO)," European Commission, Enterprise and Industry Directorate-General, Bruxelles, 2010.
- [21] Claus J. Nielsen, "PFOA Isomers, Salts and Precursors. Literature study and evaluation of physico-chemical properties.," Dept of Chemistry, University of Oslo, Klif project no. 3012013 2944/2012, 2012.
- [22] Lena Vierke, Claudia Staude, Annegret Biegel-Engler, Wiebke Drost, and Christoph Schulte, "Perfluorooctanoic acid (PFOA) main concerns and regulatory developments in Europe from an environmental point of view," *Environmental Sciences Europe*, vol. 24:16, pp. 1-11, 2012.
- [23] Rajesh R. Melkote, Liangzhen Wan, and Nicolas Robinet, "Next Generation Fluorine-Free Firefighting Foams," in 2012 Suppression, Detection and Signaling Research and Applications Symposium (SUPDET 2012), Phoenix, Arizona, 2012.
- [24] United Nations Industrial Development Organization, "Guidance on best available techniques and best environmental practices for the use of perfluorooctane sulfonic acid (PFOS) and related chemicals listed under the Stockholm Convention on Persistent Organic Pollutants," Guideline 2012.
- [25] Hans-Joachim Lehmler, "Synthesis of environmentally relevant fluorinated surfactants—a review," *Chemosphere*, vol. 58, no. 11, pp. 1471-1496, March 2005.
- [26] Civil Aviation Authority (United Kingdom), "Fire Fighting Foam IP-04, Aviation Fire Fighting Foam Performance Testing and Environmental Impact," Information Paper 2012.
- [27] Kurunthachalam Kannan, "Perfluoroalkyl and polyfluoroalkyl substances: current and future perspectives," *Environmental Chemistry*, vol. 8, pp. 333-338, 2011.
- [28] Siwen Wang et al., "First Report of a Chinese PFOS Alternative Overlooked for 30 Years: Its Toxicity, Persistence, and Presence in the Environment," *Environmental Science and Technology*, vol. 47, pp. 10163-10170, 2013.
- [29] Zhanyun Wang, Ian T. Cousins, Martin Scheringer, and Konrad Hungerbuehler, "Hazard assessment of fluorinated alternatives to long-chain perfluoroalkyl acids (PFAAs) and their precursors: Status quo, ongoing challenges and possible solutions," *Environmental International*, vol. 75, pp. 172-179, (Submitted Nov 2014) 2015.
- [30] U.S. Environmental Protection Agency, "Premanufacture Notification Exemption for Polymers; Amendment of Polymer Exemption Rule to Exclude Certain Perfluorinated Polymers," *Federal Register*, vol. 75, no. 17, p. 4295, 2010.
- [31] Australian and New Zealand Environment and Conservation Council, *Australian And New Zealand Guidelines For Fresh And Marine Water Quality.*, 2000.
- [32] Civil Aviation Authority (United Kingdom), "Foam and the environment IP6, Information for purchasers of fire fighting foam on the environment," Information Paper 2008.
- [33] John H. Duffus, Monica Nordberg, and Douglas M. Templeton, "IUPAC GLOSSARY OF TERMS USED IN TOXICOLOGY, 2nd EDITION," *Pure and Applied Chemistry*, vol. 79, no. 7, pp. 1153-1334, 2007.
- [34] Michelle M. MacDonald, P.K. Sibley, M.J.A. Dinglasan, and K.R. Solomon, "AQUATIC TOXICITY OF FLUOROTELOMER ACIDS," in *Fluoros International Symposium on Fluorinated Organics*, Toronto, Ontario, 2005.
- [35] Mei-Hui Li, "Toxicity of Perfluorooctane Sulfonate and Perfluorooctanoic Acid to Plants and Aquatic Invertebrates," *Environmental Toxicology*, vol. 24, pp. 95-101, 2008.
- [36] Safe Work Australia, "Preparation of Safety Data Sheets for Hazardous Chemicals-Code of

- Practice," ISBN 978-0-642-33311-7, 2011.
- [37] Daniel Borg, Bert-Ove Lund, Nils-Gunnar Lindquist, and Helen Håkansson, "Cumulative health risk assessment of 17 perfluoroalkylated and polyfluoroalkylated substances (PFASs) in the Swedish population," *Environment International*, vol. 59, pp. 112-123, 2013.
- [38] U.S. Environmental Protection Agency, "Long-Chain Perfluorinated Chemicals (PFCs) Action Plan," 2009.
- [39] U.S Dept of Health and Human Services, "Draft Toxicological profile for perfluoroalkyls," 2009.
- [40] Carla A. Ng and Konrad Hungerbühler, "Bioaccumulation of Perfluorinated Alkyl Acids: Observations and Models," *Environmental Science and Technology*, vol. 48, p. 4637–4648, 2014.
- [41] Environment Canada Health Canada, "Screening Assessment Report Perfluorooctanoic Acid, its Salts, and its Precursors," 2012.
- [42] German Federal Environment Agency, "Do without perfluorinated chemicals and prevent their discharge into the environment," Chemicals, 2009.
- [43] Lena Vierke et al., "Air concentrations and particle—gas partitioning of polyfluoroalkyl compounds at a wastewater treatment plant," *Environmental Chemistry*, vol. 8, pp. 363-371, 2011.
- [44] M. Pabon and J.M. Corpart, "Fluorinated surfacants: synthesis, properties, effluent treatment," *Journal of Fluorine Chemistry*, vol. 114, pp. 149-156, 2002.
- [45] Aina Marie Nordskog, "Leaching of PFCs from soil polluted by firefighting activities," University of Oslo, Oslo, Norway, Masters Thesis, Department of GeoSciences 2012.
- [46] Caroline Moermond et al., "PBT Assessment Using the Revised Annex XIII of REACH: A Comparison With Other Regulatory Frameworks," *Integrated Environmental Assessment and Management*, vol. 8, no. 2, pp. 359-371, 2011.
- [47] Myung Hee Kim, Ning Wang, and Kung Hui Chu, "6:2 Fluorotelomer alcohol (6:2 FTOH) biodegradation by multiple microbial species under different physiological conditions," *Applied Microbiology and Biotechnology*, vol. ENVIRONMENTAL BIOTECHNOLOGY, no. DOI 10.1007/s00253-013-5131-3, 2013.
- [48] Jinxia Liu and Sandra Mejia Avendaño, "Microbial degradation of polyfluoroalkyl chemicals in the environment: A review," *Environment International*, vol. 61, pp. 98-114, 2013.
- [49] Jan Zalasiewicz, "Our brave new world," New Scientist, no. 2994, pp. 26-27, November 2014.
- [50] A.R. Ravishankara, S. Solomon, A. A. Turnipseed, and R.F. Warren, "Atmospheric Lifetimes of Long-Lived Halogenated Species," *Science*, vol. 259, pp. 194-199, 1993.
- [51] D O'Hagan, "Understanding Organofluorine Chemistry. An Introduction to the C–F Bond," *Chemical Society Reviews*, vol. 37 (2) , pp. 308–319. , 2008.
- [52] Thorsten Stahl, Daniela Mattern, and Hubertus Brunn, "Toxicology of perfluorinated compounds," *Environmental Sciences Europe*, vol. 23:38, pp. 1-52, 2011.
- [53] Environment Agency (United Kingdom), "PFOS Fire Fighting Foams-Use and disposal information," Guideline 2011.
- [54] Basel Convention Secretariat–John Vifgen; Dr Ir. Ron McDowall, "Cement Kiln Co-Processing (High Temperature Treatment)," Pesticides Treatment Technology Fact Sheet 2008.
- [55] Secretariat of the Stockholm Convention on Persistent Organic Pollutants, "Guidelines on best available techniques and provisional guidance on best environmental practices relevant to Article 5 and Annex C of the Stockholm Convention on Persistent Organic Pollutants," (Cement kilns firing hazardous waste) 2008.
- [56] Mark H. Russell, Helena Nilsson, and Robert C. Buck, "Elimination kinetics of perfluorohexanoic acid in humans and comparison with mouse, rat and monkey," *Chemosphere*, vol. XXX, pp. xxx-xxx, 2013 in press.
- [57] Kavitha Dasu, Jinxia Liu, and Linda S. Lee, "Aerobic Soil Biodegradation of 8:2 Fluorotelomer Stearate," *Environmental Science and Technology*, p. 3831–3836, 2012.

- [58] THE EUROPEAN COMMISSION, "COMMISSION REGULATION (EU) No 757/2010 of 24 August 2010 amending Regulation (EC) No 850/2004 of the European Parliament and of the Council on persistent organic pollutants as regards Annexes I and III," *Official Journal of the European Union*, vol. L 223, pp. 29-36, 2010.
- [59] Changhui Liu, Karina Y. H. Gin, Victor W. C. Chang, Beverly P. L. Goh, and Martin Reinhard, "Novel Perspectives on the Bioaccumulation of PFCs—the Concentration Dependency," *Environmental Science and Technology*, vol. 45, pp. 9758–9764, 2011.
- [60] OECD Environment, Health and Safety, Environment Directorate, "Synthesis paper on per- and polyfluorinated chemicals (PFCs)," OECD/UNEP, 2013.
- [61] Melissa M. Schultz, Christopher P. Higgins, Carin A. Huset, Richard G. Luthy, and Douglas F. Barofsky, "Fluorochemical Mass Flows in a Municipal Wastewater Treatment Facility," Environmental Science and Technology, vol. 40, pp. 7350-7357, 2006.
- [62] Melissa M. Schultz, Douglas F. Barofsky, and Jennifer A. Field, "Quantitative Determination of Fluorinated Alkyl Substances by Large-Volume-Injection LC/MS/MS—Characterization of Municipal Wastewaters," *Environmental Science and Technology*, vol. 40, no. 1, pp. 289–295, 2006.
- [63] Emily Awad et al., "Long-Term Environmental Fate of Perfluorinated Compounds after Accidental Release at Toronto Airport," *Environmental Science and Technology*, vol. 45, pp. 8081-8089, 2011.
- [64] OSPAR CONVENTION FOR THE PROTECTION OF THE MARINE ENVIRONMENT OF THE NORTH EAST ATLANTIC, "OSPAR Guidelines for Completing the Harmonised Offshore Chemical Notification Format (HOCNF)," OSPAR Commission, OFFSHORE INDUSTRY COMMITTEE, OIC 03/15/1-E, Annex 6 (s3.11), 2003.
- [65] Norwegian Pollution Control Authority, "Screening of polyfluorinated organic compounds at four fire training facilities in Norway," (TA- 2444/2008), 2008.
- [66] R. S. Sheinson et al., "THE FUTURE OF AQUEOUS FILM FORMING FOAM (AFFF): PERFORMANCE PARAMETERS AND REQUIREMENTS," National Institute of Standards and Technology (U.S. Dept of Commerce), 2002.
- [67] Jessica D'Eon and Scott A. Mabury, "Production of Perfluorinated Carboxylic Acids (PFCAs) from the Biotransformation of Polyfluoroalkyl Phosphate Surfactants (PAPS): Exploring Routes of Human Contamination," *Environmental Science and Technology*, vol. 41, pp. 4799-4805, 2007.
- [68] Jonathan W. Martin et al., "Identification of Long-Chain Perfluorinated Acids in Biota from the Canadian Arctic," *Environmental Science and Technology*, vol. 38, pp. 373-380, 2004.
- [69] Ralph Hetzer, "Is there a future for AFFF without fluorine? Limitations and Opportunities," in Suppression, Detection and Signaling Research and Applications, Phoenix, Arizona, 2012, pp. 1-20.
- [70] EUROPEAN COMMISSION European Cemicals Bureau, "Technical Guidance Document on Risk Assessment," Institute for Health and Consumer Protection, TGD Part II EUR 20418 EN/2, 2003.
- [71] Martin Scheringer et al., "Helsingør Statement on poly- and perfluorinated alkyl substances (PFASs)," *Chemosphere*, vol. 114, pp. 337–339, 2014.
- [72] German Federal Environment Agency, "Preliminary assessment of perfluorinated surfactants (PFT) in Drinking water at the example of their lead compounds perfluoroctanoic (PFOA) and perfluoroctane sulfonic acid (PFOS)," Drinking Water Commission of the Federal Ministry of Health, 2006.
- [73] Sally S. White, Suzanne E. Fenton, and Erin P. Hines, "Endocrine disrupting properties of perfluorooctanoic acid," *J. Steroid Biochemistry and Molecular Biology*, vol. 127, pp. 16-26, 2011.
- [74] Post, Gloria B.- NJ Dept of Environmental Protection, "Perfluorinated Chemicals (PFCs) Emerging Drinking Water Contaminats and Occurrence in New Jersey Public Water Supplies," in *National Water Monitoring Conference*, Cincinnati, Ohio, 2014, pp. 1-53.
- [75] Fei Wang, Kaimin Shih, Xingwen Lu, and Chengshuai Liu, "Mineralization Behavior of Fluorine in Perfluorooctanesulfonate (PFOS) during Thermal Treatment of Lime-Conditioned Sludge," *Environmental Science and Technology*, vol. 47, p. 2621–2627, 2013.
- [76] ARCADIS (Elizabeth Hawley, Tessa Pancras & Jeffrey Burdick), "Remediation Teechnologies for

- Perfluorinated Compound's (PFCs), including PFOS and PFOA," White Paper 2012.
- [77] Buncefield Major Incident Investigation Board, "The Buncefield Incident—11 December 2005, The final report of the Major Incident Investigation Board," ISBN 978 0 7176 6270 8, 2008.
- [78] Henry Persson, "Ethanol Tank Fire Fighting," in ETANKFIRE, Kansas USA, 2011.
- [79] Cheryl A. Moody, Jonathan W. Martin, Wai Chi Kwan, Derek C. G. Muir, and Scott A. Mabury, "Monitoring Perfluorinated Surfactants in Biota and Surface Water Samples Following an Accidental Release of Fire-Fighting Foam into Etobicoke Creek," *Environmental Science and Technology*, vol. 36, pp. 545-551, 2002.
- [80] CHRISTIAAN J.A.F. KWADIJK, MICHIEL KOTTERMAN, and ALBERT A. KOELMANS, "PARTITIONING OF PERFLUOROOCTANESULFONATE AND PERFLUOROHEXANESULFONATE IN THE AQUATIC ENVIRONMENT AFTER AN ACCIDENTAL RELEASE OF AQUEOUS FILM FORMING FOAM AT SCHIPHOL AMSTERDAM AIRPORT," Environmental Toxicology and Chemistry, vol. 33, pp. 1761-1765, 2014.
- [81] Department of Agriculture, Fisheries and Forestry, "Queensland AgTrends 2012–13 Forecasts and trends in Queensland agricultural, fisheries and forestry production," CS 0923 09/11, 2012.
- [82] Sean Pascoe, Amar Doshi, Quentin Dell, Mark Tonks, and Rob Kenyon, "Economic value of recreational fishing in Moreton Bay and the potential impact of the marine park rezoning," *Tourism Management*, vol. 41, pp. 53-63, 2014.
- [83] Dr Stephen Wesche, Dr Tim Lucas, Dr David Mayer, David Waltisbuhl, and Dr Ross Quinn, "Gladstone Harbour Fish Health Investigation 2011–2012," Qld Dept of Agriculture Fisheries and Forestry, 2013.
- [84] Australian Maritime Safety Authority, "THE RESPONSE TO THE Global Peace OIL SPILL REPORT OF THE INCIDENT ANALYSIS TEAM," Australian Government, 2006.
- [85] Helena Nilsson et al., "Biotransformation of fluorotelomer compound to perfluorocarboxylates in humans," *Environment International*, vol. 51, pp. 8-12, 2013.
- [86] Sally S. White, Suzanne E. Fenton, and Erin P. Hines, "Endocrine disrupting properties of perfluorooctanoic acid," *Journal of Steroid Biochemistry and Molecular Biology*, vol. 127, no. 1-2, pp. 16-26, 2011.
- [87] Donald R. Taves, "Evidence that there are Two Forms of Fluoride in Human Serum," *Nature*, vol. 217, pp. 1050-1051, March 1968.
- [88] Kate Hoffman, Thomas F. Webster, Marc G. Weisskopf, Janice Weinberg, and Verónica M. Vieira, "Exposure to Polyfluoroalkyl Chemicals and Attention Deficit/Hyperactivity Disorder in U.S. Children 12–15 Years of Age," *Environmental Health Perspectives*, vol. 118, no. 12, pp. 1762-1767, 2010.
- [89] Jack Thompson et al., "Removal of PFOS, PFOA and other perfluoroalkyl acids at water reclamation plants in South East Queensland Australia," *Chemosphere*, vol. 82, pp. 9-17, 2011.
- [90] Bayerisches Landesamt für Umwelt, "Leitlinien zur vorläufigen Bewertung von PFC-Verunreinigungen in Wasser und Boden," Augsburg, Bavaria, Guideline 2013.
- [91] NICNAS Dr Kerry nugent, "Regulatory actions and risk management activities Australia," in Workshop on Managing Perfluorinated Chemicals and Transitioning to Safer Alternatives, Geneva, Switzerland, 2009.
- [92] ExxonMobil, User's Guide to Safety Data Sheets, 2011, Version 3.
- [93] UK REACH Competent Authority, Information Leaflet Number 13 Safety Data Sheets, 2012.
- [94] S. Deacon, A. Goddard, and N. Eury, "Assessing risks to ecosystems and using a net environmental benefit analysis framework to assist with environmental decision-making," in *Restoration and Recovery: Regenerating land and communities*, Howard R. Fox and Heather M. Moore, Eds.: Whittles Publishing ISBN 978-184995-012-1, 2010, pp. 164-175.
- [95] David Painter, "The Buncefield Incident experiences and lessons," in Civil Defence Symposium & Expo, http://www.alnimrexpo.com/ifpc/download/The%20Buncefield%20Expolsion%20&%20Fire_Dr.%20D

- avid%20Painter.pdf, 2014.
- [96] Parkan Behayeddin, Garry Martin, and Australia Scientific Fire Services Pty Ltd, "The Coode Island Fire Incident and its Consequences," in *Civil Defence Symposium & Expo*, http://www.alnimrexpo.com/ifpc/download/COODE%20Island%20Fire%20Incident_ParkanB.pdf, 2014.
- [97] Department of Defence (per Parsons Brinckerhoff), "Offsite Risk Assessment, PFOS and PFOA in Groundwater: Stage 3 Risk Assessment and Remediation Design, Army Aviation Centre Oakey," 2013.
- [98] Arlene Blum et al., "The Madrid Statement on Poly- and Perfluoroalkyl Substances (PFASs)," in Dioxin 2014 Symposium, Madrid, 2014.
- [99] MICHELLE M. PHILLIPS, MARY J.A. DINGLASAN-PANLILIO, SCOTT A. MABURY, KEITH R. SOLOMON, and PAUL K. SIBLEY, "CHRONIC TOXICITY OF FLUOROTELOMER ACIDS TO DAPHNIA MAGNA AND CHIRONOMUS DILUTUS," *Environmental Toxicology and Chemistry*, vol. 29, no. 5, pp. 1123-1131, 2010.
- [100] Martinsen, Kine Norwegian Climate and Pollution Agency, "Polyfluorinated compounds at fire training facilities Assessing Contaminated soil at 43 Norwegian airports," in *Common Forum on Contamionated land in the European Union*, Bilbao, Spain, 2012, pp. 1-11.
- [101] Environment Canada, "Information Regarding AQUEOUS FILM-FORMING FOAMS in Relation to the Perfluorooctane Sulfonate and its Salts and Certain Other Compounds Regulations," ISBN: 978-1-100-99097-2, 2012.
- [102] Ning Wang et al., "6:2 Fluorotelomer sulfonate aerobic biotransformation in activated sludge of waste water treatment plants," *Chemosphere*, vol. 82, pp. 853-858, 2011.
- [103] Helena Nilsson et al., "A Time Trend Study of Significantly Elevated Perfluorocarboxylate Levels in Humans after Using Fluorinated Ski Wax," *Environmental Science and Technology*, vol. 44, pp. 2150-2155, 2010.
- [104] U.S. Environmental Protection Agency Toni Krasnik, "2010/15 PFOA Stewardship Program Overview and Update," in *Workshop on Managing Perfluorinated Chemicals and Transitioning to Safer Alternatives*, Geneva Switzerland, 2009.
- [105] E.I du Pont de Nemours and Company, "DuPont Capstone 1183 (& 1157) Technical Information," Wilmington, DE, H-97566-2 & H-97584, 2008.
- [106] DuPont U.S.A., "DuPont™ Capstone® Fluorinated Surfactant 1157D Technical Information," K-25182-1 (05/12), 2012.
- [107] Stchur P, Szostek B, Bachmura SF, Rowand RC, Prickett KB, Korzeniowski SH, Buck RC. Larsen BS1, "Method development for the determination of residual fluorotelomer raw materials and perflurocatanoate in fluorotelomer-based products by gas chromatography and liquid chromatography mass spectrometry.," *Journal of Chromatography A*, vol. 1110, no. 1-2, pp. 117-124, 2006.
- [108] Kathleen Shelton, "DuPont Approach to PFOA Stewardship Exposure Reduction," in *UNEP Workshop on Managing Perfluorinated Chemicals and Transitioning to Safer Alternatives*, 2009.
- [109] Dirk Blunk, Ralf Helmut Hetzer, Angela Sager-Wiedmann, and Kai Wirz, "Siloxane-containing fire extinguishing foam," Application WO2013034521A1/EP 2753403 A1, July 16, 2014.
- [110] Ralf Helmut Hetzer, Felix Kümmerlen, Kai Wirz, and Dirk Blunk, "Fire Testing a New Fluorine-free AFFF Based on a Novel Class of Environmentally Sound High Performance Siloxane Surfactants," in FIRE SAFETY SCIENCE-DRAFT PROCEEDINGS OF THE ELEVENTH INTERNATIONAL SYMPOSIUM, Canterbury, New Zealand, 2014, pp. 1-10.
- [111] Ralf Hetzer, Dirk Blunk, Verena Hack, and Kai Wirz, "Extinguishing Foams of the Future Powerful and Environmentally Friendly," German Federal Ministry of Defence, 2011 Annual Military Scientific Research Report 2011.
- [112] Wen-Jun Hong et al., "Distribution, source, fate and bioaccumulation of methyl siloxanes in marine environment." *Environmental Pollution*, vol. 191, pp. 175-181, 2014.

- [113] Patrick Novak (CARO Analytical Services), "Siloxanes: Quantifying a New Emergent Pollutant in Water, Air and Soil," in *RemTech 2013*, Banff, 2013, pp. 1-25.
- [114] De-Gao Wang, Warren Norwood, Mehran Alaee, Jonathan D. Byer, and Samantha Brimble, "Review of recent advances in research on the toxicity, detection, occurrence and fate of cyclic volatile methyl siloxanes in the environment," *Chemosphere*, vol. 93, pp. 711-725, 2013.
- [115] Katrine Borgå, Eirik Fjeld, Amelie Kierkegaard, and Michael S. McLachlan, "Consistency in Trophic Magnification Factors of Cyclic Methyl Siloxanes in Pelagic Freshwater Food Webs Leading to Brown Trout," *Environmental Science and Technology*, vol. 47, p. 14394–14402, 2013.
- [116] Daryl J. McGoldrick et al., "Concentrations and trophic magnification of cyclic siloxanes in aquatic biota from the Western Basin of Lake Erie, Canada," *Environmental Pollution*, vol. 186, pp. 141-148, 2014.
- [117] Sharon C. Surita and Berrin Tansel, "Emergence and fate of cyclic volatile polydimethylsiloxanes (D4, D5) in municipal waste streams: Release mechanisms, partitioning and persistence in air, water, soil and sediments," *Science of the Total Environment*, vol. 468-469, pp. 46-52, 2014.
- [118] Bradley Williams et al., "Extinguishment and Burnback Tests of Fluorinated and Fluorine-free Firefighting Foams with and without Film Formation," in *Suppression, Detection and Signalling Research and Applications- A Technical Working Conference*, Orlando, Florida USA, 2011, pp. 1-15.
- [119] Wall Street Journal The Middle Seat Terminal Blog, Airports + Fire-Fighting Foam = 4:30 Friday Afternoon (Foam system test cleanup), 2008.